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SECOND INTERNATIONAL CONFERENCE ON GROUND WATER QUALITY RESEARCH

PROCEEDINGS

Edited by

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PREFACE

Water, the very essence of life, is finally achieving a level of recognition in society that it richly deserves. Simplicit in formula, it constitutes the most important natural resource essential for maintaining life and livelihood—for man's very existence is dependent on this small molecule. For years, scientists have studied the pollution and contamination of ground water, but the interpretable impact upon man and society now presents new and exciting challenges. Only recently has public concern over the quality of ground water in the United States and other countries become pronounced. The last decade has generated within the public increasing awareness of the potential problems of ground water pollutants and contaminants. State, local and federal agencies have responded by coordinating efforts to gather information about the health effects of exposure to contaminants and to develop a scientific foundation on which to base future policy decisions. Many ground water quality issues are also closely related to policies regarding ground water quantity and allocation. Predictive risk assessment is, in general, accepted by the scientific community as the only currently available method for evaluating the impact of exposure to chemical contaminants and toxic materials under existing conditions.

The Second International Conference on Ground Water Quality Research emphasized physical, chemical and biological processes that control the movement and fate of contaminants in the subsurface. New and improved processes and methodologies were discussed and coordinated with biotic and abiotic molecular transformation processes. Transport processes and sorption procedures exhibited new concepts and philosophies. The Conference provided a unique opportunity for interaction among scientists from many nations that will ultimately have global appeal and universal impact. The data and research evaluations and discussions greatly contributed to expanding the existing knowledge base—as well as providing a foundation from which future policy statements may be better formulated. The information presented in this proceeding should be meaningful to scientists presently involved in water quality research programs as well as individuals in other disciplines who may be able to apply new techniques and methodologies to resolving many of the existing problems.

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BIOLOGICAL TRANSFORMATION PROCESSES

GROUND WATER QUALITY PROTECTION—THE ISSUE IN PERSPECTIVE

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ABSTRACT

The importance of protecting ground-water resources cannot be overstated, and many people throughout the world seem anxious to physically and financially support a rational program to this end. The complacency of the public regarding the quality of ground-water was destroyed with headline-grabbing incidents of pollution such as Love Canal, Valley of the Drums, and Times Beach. Contrary to earlier popular belief, the soil mantle has been shown to be ineffective in the cleansing of certain pollutants from the water flowing through it.

The legislative basis for developing and implementing broad ground-water quality protection programs exists, although it is dispersed in a variety of pieces of legislation. Such programs presuppose the existence of the scientific knowledge necessary to produce viable and effective results from its implementation. This article addresses the research needed for accumulation of this scientific knowledge.

The issue of ground-water quality protection is before the Nation and the Congress. Accounts of contamination incidents are carried in many of our major metropolitan newspapers and national news magazines. In recent months, TV news coverage of ground-water pollution has been on the rise including several nationally televised documentaries on the occurence and movement, and the pollution of ground water. The list of contaminated sites resulting from past waste disposal practices seems to be increasing at an alarming rate. The Environmental Protection Agency has identified 546 hazardous sites to date as candidates for remedial action. Four hundred of these pose some threat to underground sources of drinking water. Every year billions of tons of solid waste are discarded in the United States. These wastes range in nature from common household trash to complex materials in industrial wastes, sewage sludge, agricultural residues, mining refuse, and pathological wastes from institutions such as hospitals and laboratories. Each year, industries alone treat 5,000 billion gallons of effluent. One thousand seven hundred (1,700) billion gallons of this go into oxidation ponds or lagoons for treatment. Based on estimated leakage rates, 100 billion gallons will leave the ponds and lagoons each year and enter the ground-water system. Of the estimated 18,500 municipal landfills in the United States in 1977, most were open dumps or were poorly sited (USEPA, 1977). The U.S. Environmental Protection Agency (EPA) estimated that in 1980 57 million metric tons of the Nation's total wasteload could be classified as hazardous. Unfortunately, many of the dangerous materials that we have "thrown away" over recent decades have persisted in the environment—making households words of "Love Canal," "Valley of the Drums," and "Times Beach." These incidents are not unique. There are hundreds of documented cases of environmental damage resulting from improper disposal or management of hazardous wastes. The vast majority of these cases involve pollution of ground water—the source of drinking water for over half of the U.S. population (USEPA, 1980). Despite heightened public concern and an advanced body of scientific knowledge relating to the occurrence and movement of ground water, it probably remains the most misunderstood of our major natural resources by the general public who often envisions underground streams or large underground reservoirs similar to surface impoundments.

It is apparent that government at all levels is anxious to address the issue of ground-water pollution and ground-water quality protection. It should also be clear that an effective program for ground-water protection must include not only a workable legal framework for administration, but also a sound scientific understanding of the occurrence and movement of ground water and the behavior of contaminants in the subsurface environment. The following review may help in placing the issues in proper perspective.

Ground water is a valuable resource because of both quality and availability. It is available in most locations in quantities large enough to provide for domestic needs; 50 percent of the population of the United States is dependent on ground water for drinking water sources. In fact, 90 percent of our rural population is dependent on ground water and it supplies 25 percent of all the fresh water used for all purposes in the United States (Josephson, 1980). Our ground-water resources are enormous. This Country's fresh ground-water supply, within one-half mile of the earth's surface, constitutes about 150 trillion cubic meters or roughly 4 times the volume of the Great Lakes (Burmaster, 1982). Ground water is a reliable resource not subject to extremes in temperature or quality fluctuations, and it is buffered from floods and droughts which affect surface supplies. Development of ground water has little effect on land use and can usually be accomplished at relatively low costs compared to surface supplies (USEPA, 1977).

This expansive nature of ground water is paradoxical in terms of its ability to meet water supply requirements over long periods of time. On the one hand, ground water is available in various quantities nearly everywhere; on the other hand it is subject to contamination from a host of sources including surface impoundments, landfills, agriculture, leaks and spills, land disposal of wastes, septic tanks, mining, petroleum and gas production and storage, underground injection of wastes, and other miscellaneous activities.

The subsurface environment is a complex system subject to extensive physical, chemical, and biological variations within small vertical or horizontal distances. This complexity is profoundly accentuated on a macro scale in terms of the multiplicity of materials comprising aquifer and soil systems. Clays, sands, silts, loams, and the various rocks and organic residues which constitute the subsurface matrix each play a unique role in water supply and waste disposal systems.

An extended period of time is usually required for movement of a pollutant from the land surface through the soil profile to underlying ground water. The overland movement of pollutions from a source to a stream or lake may require only hours or at the most a few days, but in the subsurface the movement to the ground water may take weeks or, in some cases, even years. This transport time is dependent on many variables including rainfall occurrence, intensity and duration, subsurface physical properties that control percolation rates and the nature of interactions between the pollutant and the subsurface materials. Thus, activities that involve introduction of chemicals to the land surfaces may continue for many years before the pollutants are detected in the ground water. In fact, in some cases, the pollutant sources may be gone and forgotten before the ground-water problems become apparent.

Because of the protracted effects of contamination and problems of accessibility, the restoration of underground-water quality is difficult and expensive with costs generally exceeding the short-term value of the resource as compared to the costs of alternatives. For this reason, it is widely agreed that the most viable approach to ground-water quality protection is one of prevention rather than cure (Kerns, 1977).

While the existence of our ground-water contamination problems can not be denied, the very nature of the ground-water environment and the extremely slow rate of movement of ground water tend to limit the spread of pollutants in the subsurface and ameliorate the severity of the problem. Although evidence of ground-water contamination is found in many places, the volume of ground water contaminated is small compared to the enormity of the resource. Available estimates suggest that only a few percent of available ground-water resources, at most, have been contaminated. As would be expected, however, most of the polluted ground water occurs in areas of high population density and high demand for the resource. Aquifers already contaminated may, however, remain so for a long period because practical technology for purifying them has only recently been under development.

Historically, environmental legislation has been directed at tightening controls on that pollution which has directly assaulted our senses. Trash floating in harbors and rivers causing obstruction to navigation inspired the first piece of Federal environmental legislation—the Rivers and Harbors Act of 1899. While this initial act is still in effect and has served as the basis for waste discharge permits issued by the Corps of Engineers and EPA, Federal authority for addressing ground-water quality problems is now embodied in at least eight statutes. Ironically, much of the environmental legislation of the past, and the present, may actually have the effect of shifting pollution loads from the air, rivers and oceans to the soil and ultimately to ground water (USEPA, 1977).

The Water Pollution Control Act of 1956 was amended over the years, evolving into the Federal Water Pollution Control Act in 1972 and the Clean Water Act in 1977. This act is aimed primarily at pollution control of navigable waters with the eventual goal of elimination of waste discharges to these systems. The Clean Water Act provides for State water quality management programs that may address ground water.

The National Environmental Policy Act of 1970 requires that Environmental Impact Statements be prepared for projects that might have significant adverse effects on the environment, including ground water.

Ground-water protection under the Safe Drinking Water Act is implemented through drinking water regulations, underground injection control regulations, and the sole source aquifer program.

At present these are drinking water standards which establish maximum contaminant levels for ten inorganic chemicals, ten organic chemicals (including six pesticides), microbiological contaminants, radio nuclides, and other contaminants found in ground water. In addition, there is a four-phase plan for promulgation of new regulations.

Under the underground injection control program, underground injection of materials that pose a threat to ground water is regulated. This program ensures that injection well activities do not endanger present and future sources of drinking water.

Lastly, the sole source aquifer program permits citizens to petition EPA for designation of an area as a sole source if it is a principal water supply. To date 11 aquifers have been designated and an additional 22 petitions are being reviewed. This designation provides for EPA review of all Federally funded projects that may affect the quality of ground water in a sole source aquifer.

The Toxic Substances Control Act addresses ground-water contamination issues under three sections. Under Section 4, the Agency may require testing of chemical substances to determine whether they pose unreasonable risks to human health or the environment. Under Section 5, manufacturers of chemicals are required to notify the Agency before beginning production of new chemicals, or before beginning production of a chemical for a significant new use. Under Section 6, the Agency can take various regulatory actions against chemicals which present an unreasonable risk to human health and the environment.

Under Subtitle C of the Resource Conservation and Recovery Act (RCRA), EPA has promulgated regulations which provide "cradle to grave" management of hazardous waste. Operators of land disposal facilities (approximately 1400) are required to monitor for potential ground-water contamination. New facilities must have underliners and leachate collection systems. Corrective action is required in the event of ground-water contamination at permitted facilities.

The Surface Mining Control and Reclamation Act of 1977 has provisions aimed at the prevention of chemical contamination and hydrological disruption of ground water.

The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) is a licensing statute which permits EPA to restrict the use of hazardous pesticides, and to cancel or suspend the registrations of pesticides that pose the risk of unreasonable adverse effects to humans or the environment. FIFRA gives the Agency significant discretion in dealing with possible contamination of ground water by pesticides.

In 1980, Congress enacted the Comprehensive Environmental Response, Compensation, and Liability Act which authorizes government responses to spills of hazardous substances as well as clean-up of abandoned hazardous waste sites. The Act defines "environment" to include ground water and establishes a $1.6 billion trust fund to finance government responses to releases or threats of releases of hazardous substances that may harm human health or the environment.

State attention to ground-water quality, like the Federal situation, has generally taken a low priority compared to surface water. This is further complicated by the complexities and diversity of ground-water ownership from one part of the Country to another.

The protection of ground-water quality in most states is gained from statutes dealing with surface water which generally are based on public health (USEPA, 1977). Land-use regulations are also used to protect ground-water quality by locating waste sources, such as lagoons and solid waste facilities, in areas to minimize the pollution potential.

Construction regulations are often used in a secondary manner to protect ground water. For example, water wells are constructed primarily to prevent contamination of the well with little thought given to protecting the area's ground water. Septic tank regulations are aimed specifically at controlling surface discharges, disease, and nuisance in much the same way as landfills are designed to prevent smoke, odors, rodents, and unsightliness.

The only technically or economically viable option now available for protection of ground-water quality on a broad scale is prevention of contamination (Kerns, 1977).

One simple approach would be to ban, from the recharge zone, all land use practices that could contribute pollutants to the aquifer. While this might work in some instances it simply cannot be adopted totally in any practical way. The community of man will continue to produce waste products as a result of those activities deemed necessary to support a contemporary standard of living, and those wastes must be managed with considerable thought given to economics.

Some wastes, due to their high inherent toxicity, should probably not be disposed of on the land. For these, incineration, eternal encapsulation or deep well injection offer the principal management options. For other less hazardous chemicals nature itself can provide economical treatment alternatives to render them environmentally acceptable. The key is to understand the natural physical, chemical and biological processes which control the transport and transformation of contaminants in the subsurface so that we can manage the system and utilize its natural assimilative capacity in such a way as to provide effective protection to ground water without unnecessarily restricting other land use activities.

A research strategy designed to provide the technical information required by a viable ground-water protection program has been developed over the past few years through involvement of the U.S. Environmental Protection Agency and other public and private organizations.

This requires developing the scientific knowledge of pollutant behavior in the subsurface that permits intelligent management of ground-water resources. Management considerations include the ability to identify, evaluate, and control potential sources of ground-water contamination; to assess the risks and impacts associated with emergency spill situations and other contamination events; and to take remedial action in the restoration of ground-water quality.

The processes that govern the behavior of pollutants in the subsurface can be divided for research purposes into three major areas: (1) hydrologic, (2) abiotic, and (3) biotic. These processes will act to influence the movement of water, the primary vehicle for subsurface pollutant movement; the physical and chemical interactions that will cause pollutants to move at rates different from those of the water; and chemical or microbial alterations that will remove pollutants from the subsurface or render them to insoluble constituents at the surface matrix. The elucidation of the importance and magnitude of the various mechanisms functioning in the three process areas will ultimately provide the knowledge to integrate the influences of these processes into a singular understanding of pollutant behavior in the subsurface. Research under each of these process areas is organized into a series of tasks focusing on methods development, subsurface characterization, pollutant attenuation, process kinetics, field application and mathematical model development and application.

Efforts in hydrologic processes are primarily directed toward two aspects: (1) the influence of the physical and chemical features of the subsurface on the movement of fluids and accompanying contaminants through it, and (2) mathematical descriptions of the processes that control this movement (Ground-Water). The results of this research will be used to predict the movement of contaminants in order that ground-water monitoring procedures can be developed.

The abiotic processes of primary concern in the subsurface environment are sorption/partitioning and chemical degradation. Emphasis to date has been on the sorption process. Gaining a predictive understanding of the sorbate, sorbent, and solution characteristics that affect the rate and degree of sorption will permit refinement of models describing transport and fate of pollutants in the subsurface.

Research efforts in the biotic processes category are focused on developing necessary information to predict the transport, fate, and impact of pollutants in the subsurface and to develop control and remedial technology for ground water quality. Considerable progress has been made in recent years in developing methods for obtaining uncontaminated samples, in developing new techniques and procedures for characterizing subsurface biota, and in developing technology for determining how biological processes affect pollutant transport and fate (Scalf).

Current information indicates that the deeper subsurface environment is not sterile and that there may be considerable spatial variation in microbial populations both from a qualitative and quantitative standpoint (EOS, 1983). These conclusions, however, are based on a very limited number of studies and far more information on the distribution, density, and nature of organisms in the subsurface, both above and below the water table, is needed. Future studies should emphasize correlating the occurrence and activities of organisms with the geological and mineralogical properties and the environmental conditions of the subsurface regions where the organisms exist.

At present little is known about biodegradation of organic pollutants in the deeper subsurface. A limited amount of pollutant biodegradation research has been done using the indigenous flora of the subsurface and foreign pollutants; virtually no work has been accomplished in situ (Wilson, 1983). These results have indicated that the potential for significant biodegradation of a number of compounds exists. However, the question remains unanswered as to the degree to which these reactions will proceed in the subsurface. The limitations have not been clearly defined to be either thermodynamic or kinetic nor has the extent of adaptation and cometabolism been investigated in detail. Very little is known concerning degradation byproducts or whether degradation processes can be manipulated.

Little is known concerning environmental conditions in subsurface habitats and the effect such conditions have on biological activity and the biotic transformation of pollutants (McNabb, 1974). Important factors governing the extent and/or nature of biological activity include the concentration and utility of electron acceptors; the concentration and availability of essential nutrients; the oxidation-reduction potential; the pH; the ionic composition; the availability of water; the temperature; the hydrostatic pressure; the nature of solid phase; and the nature of the pore space. All of the above factors interact to influence the activity of organisms in the subsurface.

Biodegradability and the associated kinetic relationships must be determined prior to development and use of mathematical models for predicting the movement and fate of pollutants in the subsurface environment. Volatilization and sorption should be determined to predict biodegradation, since a mass balance is required. Reaction kinetics should be determined for modeling. Studies are required to determine: the effect of concentration of pollutant in the rate law for transformation; the effect of concentration of pollutant on the density of microbes active against that pollutant; and the correlation between the rate of transformation of the pollutant and the density of viable microbes, or the concentration of some biochemical constituent of the microbes used as an indicator of biomass or nutritional state.

To use laboratory and field information about subsurface biotic reactions to predict the fate of pollutants requires the development of mathematical submodels that describe the kinetics of biological transformations in the subsurface, and which can be incorporated into more sophisticated mass transport models describing water movement and abiotic attenuation of pollutants. Successful development of a viable biotic processes submodel will be dependent upon the determination of biotransformation kinetic information. Current mass transport models are deficient in handling biotic processes (Enfield, 1982).

An expanded knowledge of pollutant behavior in the subsurface environment is fundamental to taking effective action to prevent or limit ground-water pollution or to rehabilitate already contaminated systems. The dearth of knowledge that stems from previous public disinterest to ground-water pollution problems makes the task both arduous and expensive. To quote T. S. Eliot, "The fact that a problem will certainly take a long time to solve, and that it will demand the attention of many minds for several generations, is no justification for postponing the study" (Eliot, 1949).

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APPLICATION OF BIOLOGICAL TRANSFORMATIONS IN GROUND WATER

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ABSTRACT

Microorganisms can bring about the transformation of many common trace organic ground-water contaminants which serve as secondary substrates. Half-lives of such compounds are generally long because of low active microbial concentrations, inappropriate environmental conditions, or inability of indigenous bacteria to acclimate to the compounds. Some hazardous compounds such as chlorinated benzenes appear biodegradable only under aerobic conditions, while others such as many halogenated aliphatic compounds appear biodegradable only under anaerobic conditions. Biotransformation of some compounds, such as tetrachloroethylene, 1,1,1-trichloroethane, and ethylene dibromide, result in the transient formation of intermediates such as vinyl chloride. The impact of environmental conditions and intermediate formation needs to be better understood. Biotransformation rates might be increased through the stimulation of indigenous bacteria by injection of a suitable primary substrate and required nutrients, and by maintenance of a suitable environment. This might also result from the introduction of acclimated bacteria. However, much more needs to be known about the native microorganisms, their biochemical capabilities, and the effect of environmental conditions on biodegradation.

INTRODUCTION

Biological transformation is about the only process that can bring about the destruction of hazardous organic chemicals in ground water. Light is not available for photolysis, and the absence of contact with the atmosphere reduces the opportunity for volatilization loss. Chemical hydrolysis might occur, but for most compounds, this process is very slow. In addition, chemical hydrolysis generally results in simple transformations of one organic compound into another, while biological transformations frequently can bring about complete mineralization to harmless inorganic end products.

However, relatively little is known about microbial activity in ground water environments. Evidence is available indicating that somewhat concentrated and readily biodegradable compounds can be transformed in the subsurface environment. There is also some evidence that trace concentrations of trihalomethanes can be transformed anaerobically (Bouwer and McCarty, 1982; Roberts et al., 1982; Schwarzenbach et al., 1983). The rates of transformation are quite low, with half-lives of weeks to months. However, these rates are still more significant than that resulting from chemical transformations under an aquifer environment.

Factors affecting the rates of biological transformation of trace organic compounds are quite complex. The rates are affected by temperature, microbial concentration and activity towards a particular compound, substrate concentration, presence of microbial toxicants and nutrients, and the particular electron acceptors that may be present. Perhaps the major unknown is the potential activity of the native microflora towards transformation of individual compounds.

A significant question has been whether or not organic compounds, present at trace concentrations, can be biotransformed (Boethling and Alexander, 1979a and 1979b). At low concentrations there may not be sufficient energy available from consumption of a given compound to support bacterial growth. Also, concentrations may be too low to bring about needed enzyme induction. However, there is now sufficient evidence to indicate that microorganisms are capable of mineralizing many compounds of potential health concern down to concentrations well below 1 μg/1 (Bouwer and McCarty, 1982, 1983a, and 1984). Field evidence from studies on the fate of trace organic compounds present in reclaimed wastewaters injected into an aquifer indicates that under proper conditions trihalomethanes can be transformed with half-lives of about thirty days (Bouwer and McCarty, 1982; Roberts et al., 1982). Another study on the infiltration of aromatic hydrocarbons and chlorobenzenes into ground water from river percolation suggested that these compounds can also be transformed under proper conditions with half-lives of perhaps a few days or less (Schwarzenbach and Westall, 1981; Schneider et al., 1981). These rates are too rapid to be explained by chemical transformations, and thus are probably biological in nature.

BIOFILM PROCESSES IN GROUND WATER

A biofilm is a layer-like aggregation of microorganisms attached to a solid surface (Rittmann and McCarty, 1978). They generally result in natural systems that have a high specific surface area and low nutrient concentrations, such as would be expected in an aquifer. Factors affecting the rate of transformation of organic material by biofilms have been widely studied and are fairly well understood (Williamson and McCarty, 1976; Rittmann and McCarty, 1980a and 1981; Atkinson and Davies, 1974; Harremoës, 1978). Figure 1 depicts three different types of biofilm that may be of significance in ground water.

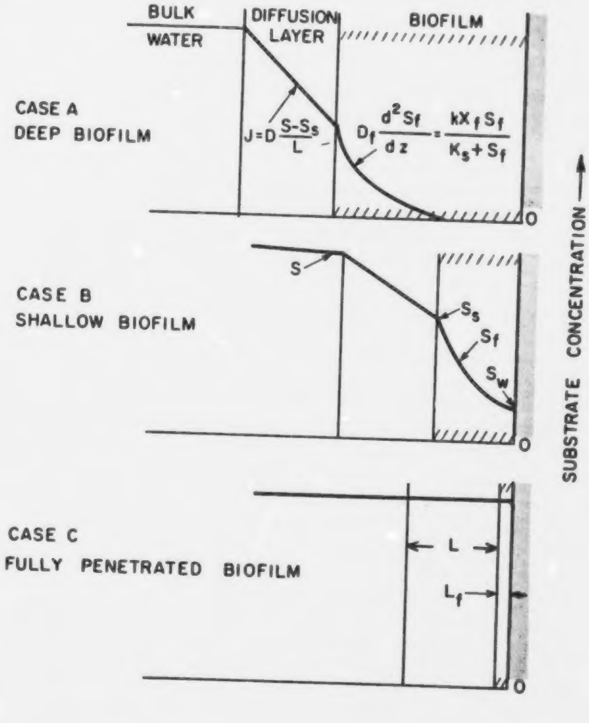

Figure 1. Substrate profiles in three types of biofilms (after McCarty et al., 1984)

In a deep biofilm substrate moves from the bulk liquid across a diffusion layer to the biofilm by mass transport. It then diffuses into the biofilm as a result of a concentration gradient, and is there transformed by the microorganisms present. The rate of transformation at any point within the biofilm is a function of substrate concentration at that location. In the deep biofilm case, the substrate concentration approaches zero at the biofilm solid-surface interface. The three main processes involved are thus mass transport from the bulk liquid to the biofilm surface, diffusion into the biofilm, and transformation within the biofilm. At temperatures of 5°C or above, half-lives of compounds in an aquifer in the presence of a deep biofilm would be on the order of minutes to hours. This may be the case near the point where a wastewater or heavily contaminated water enters a subsurface environment either by percolation or injection, resulting in heavy bacterial growth.

A shallow biofilm is one in which the substrate concentration maintains a reasonably high value at the solid-surface interface relative to the concentration (S_s) at the water interface. This occurs when the biofilm is just developing, or when the substrate concentration supporting the biofilm is very low so that the biofilm remains relatively thin. The flux or substrate into a shallow biofilm is less than that of a deep biofilm. A shallow biofilm represents the intermediate case between a deep and a fully-penetrated biofilm, and the respective half-lives for organic contaminants would lie between the two.

A fully-penetrated biofilm is very shallow and reaction rates are relatively slow compared with the rate of substrate diffusion from the bulk-liquid into the biofilm. Thus, the concentration of substrate surrounding the microorganisms is essentially the same as in the bulk liquid. Such a case may be represented by aquifer media that has a biofilm equivalent in thickness to only a few bacteria, or it may extend down to aquifer media containing no more than a few bacteria per grain of sand. Here, rates of transformation are low and half-lives of organic compounds in the order of hours to months may be expected. This is the case of significance in many contaminated aquifers. Since the rate of ground water movement is generally quite low, processes that require on the order of a few months to bring about contamination degradation can still be quite significant in helping to purify an aquifer.

Numerical models have been developed for describing the rates of reactions for a deep biofilm (Rittmann and McCarty, 1978; Williamson and McCarty, 1976; Williamson and Chung, 1975) and a shallow biofilm (Rittmann and McCarty, 1980a and 1981; Atkinson and Davies, 1974), and involve the effects of mass transfer, diffusion, and microbial transformation. With a full-penetrated biofilm, only the latter need be considered since it limits the rate of reaction. Here the rate of reaction can be assumed to follow Monod kinetics (Bouwer and McCarty, 1982):

$$-\frac{dS_f}{dt} = \frac{kXS_f}{K_s + S_f} \tag{1}$$

where:

S_f = bulk substrate concentration, mg/1
X = concentration of active bacteria, mg/1
t = time, day
k = coefficient of maximum rate of substrate utilization, day^{-1}
K_s = half-velocity coefficient, mg/1

At high substrate concentration, the rate of utilization is maximum and zero order with respect to substrate concentration:

$$-dS_f/dt = kX \quad (S_f >> K_s) \tag{2}$$

At low substrate concentration, the rate of utilization is first-order with respect to substrate concentration:

$$-ds_f/dt = (k/K_s)XS_f \quad (S_f << K_s) \tag{3}$$

For the case where the active organism concentration in the aquifer does not change significantly with time, Equation 3 can be rearranged and integrated to allow estimation of the half-life ($t_{1/2}$) for the organic compound:

$$t_{1/2} = \frac{K_s \ln 2}{kX} \quad (\frac{dX}{dt} = O,\ S_f << K_s) \tag{4}$$

For a typical case at 20°C, where $k = 10\ \text{day}^{-1}$ and $K_s = 10$ mg/1, the relationship between half-life and concentration of organisms that actively decompose the trace compound can be calculated as summarized in Table 1. In order to calculate the number of organisms per ml, it was assumed that a microbial cell has a dry weight of 2×10^{-10} mg. As temperature decreases, k generally decreases and K_s increases, generally by a factor of 2 to 3 per 10°C change. At temperatures of 5° to 10°C, half-lives may increase from those summarized in Table 1 by 4 to 25 times. Thus, temperature effects can be very important.

Table 1. Calculated Half-Lives for Biodegradable Trace Organic Compounds as a Function of Active Organism Concentration[a]

Organism Concentration		
mg/1	no./ml	$t_{1/2}$
1000	5×10^9	0.5 min
100	5×10^8	5 min
10	5×10^7	0.8 hr
1	5×10^6	8 hr
0.1	5×10^5	3.5 days
0.01	5×10^4	35 days
0.001	5×10^3	1 year
0.0001	5×10^2	10 years
0.00001	5×10^1	100 years

[a] Using typical values at 20°C for k and K_s. For lower groundwater temperatures, reaction rates are reduced and half-lives would be longer.

Ghorise and Balkwill (1983) and Wilson and McNabb (1983) have reported on microbial populations in aquifers, and found that the numbers are surprisingly high. These oligotrophic bacteria do not tend to grow in normal culture media with high substrate concentration, but can be observed microscopically to be present in aquifer material. If a ground water population of 10^6 to 10^7/ml as suggested by their data were actually active towards a particular micropollutant, then a half-life as low as one day might be expected. Half-lives with this magnitude have been observed for aromatic hydrocarbons (Roberts et al., 1982); however, the half-lives noted for chlorinated benzenes and halogenated aliphatics are much longer. A microbial population active towards a given compound and greater than about 10^5/ml of pore space would be sufficient at 20°C to bring about decomposition of trace organics at a rate that is relatively rapid with respect to the rate of movement of ground water. This population corresponds to only about one organism per grain of fine sand, a number that is quite difficult to count microscopically. If such a population size is not present in an aquifer naturally, then it may be possible to stimulate its growth by addition of a suitable substrate. This is an area worthy of investigation.

PRIMARY AND SECONDARY SUBSTRATES

In order for there to be a net growth of indigenous microorganisms in an aquifer, a substrate must be provided that permits their rate of growth to exceed their rate of decay. The net growth rate of microorganisms can be approximated by the following equation (Rittmann and McCarty, 1980a):

$$\frac{dX}{dt} = \underbrace{\frac{YkS_fX}{K_s + S_f}}_{\text{growth}} - \underbrace{bX}_{\text{decay}} \tag{5}$$

where:

Y = yield coefficient, mg cells per mg substrate
b = organism decay coefficient, day^{-1}

The minimum substrate concentration (S_{min}) is defined as that where growth just balances decay or:

$$S_{min} = \frac{bK_s}{Yk - b} \quad (dX/dt = 0) \qquad (6)$$

If a single substrate enters an aquifer, but its concentration is below S_{min}, then there can be no net growth of microorganisms and the rate of substrate utilization will not increase. However, if the concentration is greater than S_{min}, then the microbial population can increase in size, and the rate of substrate utilization should increase with time. This concept has been verified in laboratory studies on simulated aquifer material (Bouwer and McCarty, 1982; Rittmann and McCarty, 1980b; LaPat-Polasko et al., 1984). Values for S_{min} may be on the order of 0.1 to 1 mg/1, and would tend to increase with decreasing temperature. However, oligotrophic bacteria may have characteristics that permit them to have a lower S_{min} so that they can survive in nutrient deficient environments. This area is in need of further study.

Frequently, ground water contaminants are present in concentrations in the low μg/1 range, perhaps well below the S_{min} value for microorganisms. However, it has been demonstrated that if bacteria are provided with a primary substrate at a concentration greater than S_{min}, then they may be capable of degrading a trace contaminant while using it as a secondary substrate (LaPat-Polasko et al., 1984). Thus, indigenous microorganisms might be stimulated to grow in numbers through the addition of a non-harmful primary substrate such as acetate, so that their rate of utilization of a harmful substance can be increased. This possibility has been demonstrated in laboratory studies, but needs to be applied in the field.

ENVIRONMENTAL REQUIREMENTS FOR TRANSFORMATIONS

In order for microorganisms to grow, appropriate environmental conditions must be maintained. This requires, in addition to a primary substrate, sufficient inorganic nutrients such as nitrogen and phosphorus. The rates of growth and substrate utilization are dependent upon pH and temperature as well as upon limiting-substrate concentration. Contaminants in high concentration can be toxic and thus can inhibit bacteria in their growth or ability to transform compounds.

Finally, the particular microorganisms that grow and the biodegradability of a given organic compound depend upon the electron acceptors that may be present. Certain compounds are transformed by microorganisms growing in the presence of oxygen that are not transformed when it is absent. On the other hand, several common ground water contaminants appear to be biotransformed only by methanogenic mixed-cultures that live in the absence of oxygen. Others are transformed under anoxic conditions in the presence of nitrates or sulfates.

In addition, the microbial transformations themselves change the relative abundance of electron acceptors. When biodegradable organic materials are introduced into a ground water containing oxygen and microorganisms, the oxygen will be consumed along with the organic material. If sufficient organic material is introduced, then the complete utilization of the oxygen present can occur and anoxic conditions will result, bringing into action a new group of microorganisms with different potentials for hazardous organic compound transformation. Biological reactions that reduce nitrite and nitrate will occur first. When these electron acceptors are consumed, then sulfate reduction and perhaps methane fermentation can begin. Thus, as organic material enters and flows along with ground water, a series of redox zones can result varying from aerobic and highly oxidative to anaerobic and highly reductive. The extent of these redox zones can be altered by the introduction of particular electron acceptors or electron donors (biodegradable organic material) into the aquifer. The potential for such control needs to be explored.

Laboratory studies with continuous-flow columns containing glass beads and seeded with mixed bacterial cultures to simulate ground water conditions have been conducted to determine the effect of electron acceptors on the biodegradation of a range of potentially hazardous organic chemicals commonly found in ground water (Bouwer and McCarty, 1982, 1983a, 1984; Rittmann and McCarty, 1980b). The glass beads acted as the support surface for the microorganisms. In the aerobic studies, acetate at a concentration of 1 to 5 mg/l was used as the primary substrate (Bouwer and McCarty, 1984; Rittmann and McCarty, 1980b). The detention time in the column was about 20 min, and the column was seeded with settled domestic wastewater. An active biofilm soon developed that was capable of reducing the acetate to its S_{min} concentration. Table 2 indicates the time required for acclimation of the culture to the various trace organic substrates present. With some, such as styrene and napthalene, no acclimation period was required (Bouwer and McCarty, 1984). With chlorinated benzenes, an acclimation time of a week or longer was required, depending upon the structure of the given compound (Bouwer and McCarty, 1982). Carbon-14 tracer studies indicated these compounds were completely mineralized to carbon dioxide. No organic intermediates were found. However, the aerobic biofilm did not bring about transformation of the halogenated aliphatic compounds over the more than one and one-half years of this study. The acetate primary substrate was sufficiently high in concentration to develop a deep biofilm so that half-lives for the compounds were on the order of minutes.

Table 2. Laboratory Results on Biofilm Transformation of Secondary Organic Compounds Under Aerobic Conditions[a]

Compound	Initial Concentration (μg/1)	Acclimation Time (days)	Percent Biotransformed
Biotransformed			
Ethylbenzene	9	0	99
Napthalene	14	0	99
Styrene	8	0	99
Chlorobenzene	10	20	91
1,2-Dichlorobenzene	10	20	97
1,3-Dichlorobenzene	10	300	71
1,4-Dichlorobenzene	11	10	99
1,2,4-Trichlorobenzene	9	40	95
Not Transformed			
Chloroform	28	—	0
1,1,1-Trichloroethane	16	—	0
Tetrachloroethylene	10	—	0

[a] Glass bead column with 1 mg/1 acetate as primary substrate and void-volume detention time of 20 minutes (T = 20°C) (Bouwer and McCarty, 1982 and 1984; Bouwer, 1982).

A similar system was used for anaerobic, methanogenic conditions (Bouwer and McCarty, 1983a). Here, the acetate concentration was increased to between 100 and 600 mg/l, and the detention time was increased to two days. The results of these experiments are listed in Table 3. The aromatic compounds that were degradable under aerobic conditions were not degradable under these anaerobic conditions. However, the halogenated aliphatic compounds were all biodegradable under anaerobic conditions, an unexpected result.

Carbon-14 studies were conducted to determine the fate of selected haloaliphatic compounds under the methanogenic conditions. The compounds studied included chloroform, carbon tetrachloride, 1,2-dichloroethane, and 1,2-dibromoethane (commonly called ethylene dibromide or EDB). Chloroform was mineralized, primarily to carbon dioxide with some methane as was carbon tetrachloride. 1,2-dichloroethane was not transformed in the continuous-flow column, but was under batch anaerobic conditions, and primarily to carbon dioxide. EDB was rapidly transformed, but not to an inorganic end product. One of the end products formed was highly volatile from water and was not absorbed by a Tenex column. Because of the latter,

Table 3. Laboratory Results on Biofilm Transformation of Secondary Organic Compounds Under Anaerobic Conditions[a]

Compound	Initial Concentration (μg/l)	Acclimation Time (days)	Percent Biotransformed
Biotransformed			
Chloroform	33	70	96
Bromodichloromethane	30	0	>99
Dibromochloromethane	34	0	>99
Bromoform	34	0	>99
1,1,1-Trichloroethane	25	70	98
Tetrachloroethylene	18	70	86
Carbon tetrachloride[b]	17	b	>99
1,2-Dibromoethane	27	b	>99
1,1,2,2-Tetrachloroethane	27	b	97
Not Transformed			
1,2-Dichloroethane[c]	22	—	0
Ethylbenzene	12	—	0
Styrene	8	—	0
Napthalene	29	—	0
Chlorobenzene	22	—	0
1,2-Dichlorobenzene	15	—	0
1,3-Dichlorobenzene	10	—	0
1,4-Dichlorobenzene	10	—	0
1,2,4-Trichlorobenzene	11	—	0

[a] Glass bead column with 100 to 600 mg/l acetate as primary substrate and void-volume detention time of 2 days (T = 20°C) (Bouwer and McCarty, 1984; Bouwer, 1982).

[b] Compound added to column feed after 15 months, acclimation was immediate.

[c] Compound slowly degraded in batch anaerobic studies (end product was carbon dioxide), but not in column studies.

it did not appear to be halogenated. The end product appears to have been ethane, but this has not been verified positively. An intermediate compound was also formed that was not volatile and not extractable by organic solvents, thus it could have been an alcohol. This soluble end product represented about 25 percent of the initial EDB carbon after two weeks, but had decreased to about 7 percent at the end of four months.

Other intermediate compounds of signifance were found for 1,1,2,2-tetrachloroethane and tetrachloroethylene. They were changed by reductive dehalogenation to 1,1,2-trichloroethane and trichloroethylene, respectively. In this process, a halogen is removed and substituted with a hydrogen atom. In the case of tetrachloroethylene, if this process were to continue, the trichloroethylene would be transformed into dichloroethylene, and then vinyl chloride. Evidence suggests the vinyl chloride would in turn be converted into carbon dioxide. Evidence for these intermediates has been given elsewhere (Parsons et al., 1984), and we have confirmed this by unreported experiments in our own laboratories. There have been many unconfirmed-to-date reports of vinyl chloride presence in ground waters and anaerobic systems where either trichloroethylene or tetrachloroethylene were initially present. Vinyl chloride is a known human carcinogen, and its potential formation by this route is cause for some concern. This is an area where more information is needed both to help explain phenomena being observed and for understanding the needs for the protection of ground waters.

Additional batch studies have indicated that under anoxic conditions with nitrate present, some of the chlorinated aliphatics can be decomposed, but not as many as under methanogenic conditions (Bouwer and McCarty, 1983b). Those transformed include carbon tetrachloride, the brominated trihalomethanes, and 1,2-dibromoethane. Somewhat surprisingly, chloroform was noted as a decomposition product of carbon tetrachloride, although most of the carbon tetrachloride carbon was recovered as carbon dioxide.

The above studies have indicated that many of the commonly recognized ground water contaminants can be transformed under suitable conditions of active microbial population and environmental conditions. Aerobic conditions are required for some transformations and anaerobic for others. Long acclimation times are required to achieve transformation of some compounds. There is evidence that the transformations noted to take place in some aquifers, but in others, transformations do not appear to occur. More research is needed in order to determine whether a given aquifer has the potential for biotransformation of given contaminants, or whether this ability can be induced by changing the chemical characteristics of the aquifer. In situ treatment offers real potential for reducing clean-up costs and at the same time minimizing disruption of an area.

BIOCLEANING OF AN AQUIFER

Indigenous aquifer microorganisms may or may not be capable of transforming contaminants introduced into the aquifer at a given site because of the small numbers of active organisms present, genetic limitations, or environmental conditions. Methods or procedures are desirable that can be used to control or enhance the ability of microorganisms to mineralize ground water contaminants. In the following, one possible scheme is described that might be used to remove halogenated aliphatic compounds from an aquifer through biotransformation processes. A similar scheme might also be used for compounds that are aerobically biodegradable.

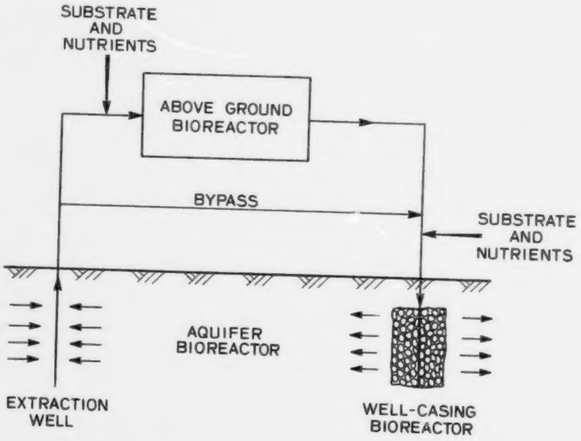

Figure 2. Possible system for generating acclimatized bacteria and biologically treating a contaminated aquifer

The proposed scheme is illustrated schematically in Figure 2. It consists of (1) an above-ground bioreactor, (2) a well-casing bioreactor, and (3) an aquifer bioreactor. Thus, the system offers three separate reactor systems in which biotransformations may take place. Contaminated ground water is pumped from the aquifer and fed to the above-ground bioreactor. Here, with the introduction of a primary substrate and biological nutrients as needed, and after a suitable acclimation time, an active microbiological population is developed and the hazardous chemicals are destroyed. The effluent from the reactor should have the proper anaerobic conditions and should contain a small seed of acclimated microorganisms. A primary substrate and nutrients are added to this water and it is injected into a large well containing a gravel packing to which the microorganisms can become attached. Contaminated aquifer water is also injected into this well. The contaminants are likely to be only partially destroyed by the bacteria that develop in the well reactor because of the relatively short detention time provided. The treated water with the proper environmental conditions, and remaining contaminant and a small concentration of acclimated microorganisms enter the aquifer environment. The correct environmental conditions for this entering water may also stimulate indigenous aquifer organisms to develop so that they can become active in transforming the remaining hazardous organic material. If they cannot, then the introduced microorganisms may slowly work their way into the aquifer to be in a position themselves to bring about the transformation. Once the indigenous or the introduced population in the aquifer develops adequately, then the above-ground reactor can be discontinued, and perhaps the well-casing reactor as well. The extracted and injected ground water would then be treated in place, with perhaps the only requirement being that adequate primary substrate and nutrients be added to maintain environmental conditions and a viable and acclimated microbial system. Certainly a great deal of development work is needed here.

If the aquifer treatment system fails to operate, then the well-casing reactor may be able to treat an adequate quantity of extracted water. If this fails, then the above-ground reactor can serve as the sole treatment system. The proposed system not only has redundancy, but also a good potential for increasing the natural rates of biodegradation in an aquifer. It is one scheme among perhaps many that might capture the natural ability of microorganisms to transform organic materials in an aquifer, thus avoiding the more costly removal schemes that are frequently proposed.

SUMMARY

There is sufficient field and laboratory evidence to indicate that microorganisms can biotransform many of the common ground water contaminants that pose a significant health risk to the public. In order to take advantage of this capability in the clean-up of ground water contaminations, much additional research is needed.

Primary among the research needs is a better understanding of the characteristics of indigenous bacteria in aquifers. What are their numbers and how does this vary from aquifer to aquifer? What is their range of physiological characteristics in a given aquifer? Is the ability to function under aerobic or anaerobic conditions, and to acclimate to the range of common ground water contaminants ubiquitous, or is it different in different aquifers? What is the range of electron acceptors that can be present or must be present for the biotransformation of each contaminant of interest to occur? For each group of microorganisms and environmental conditions that may be useful for the transformation of a given compound, what are the effects of environmental variables such as temperatures, pH, and substrate concentration on microorganism growth rates and biotransformation rates of contaminants? How does temperature affect the length of time required for acclimation and to develop a suitable population level in an aquifer? What primary substrates are best for stimulating the growth of indigenous microorganisms? How should the primary substrate be administered and what inorganic nutrients should be added along with it? If indigenous microorganisms in a given aquifer do not have the ability to transform a given contaminant, how might non-native microorganisms with this ability be introduced? What factors affect the distance to which introduced microorganisms can penetrate into an aquifer? How serious is the potential clogging problem in an aquifer that might result from the introduction of a primary substrate or microorganisms? How might such a problem be minimized? What intermediate compounds are likely to form from biotransformation and how can these be dealt with safely?

There are many more questions that might be asked and directions that can be taken in order to adequately understand and apply techniques to take advantage of the biotransformation ability of microorganisms. Perhaps most needed are field-scale studies in which attempts are made to stimulate indigenous bacteria, and where acclimated organisms are introduced. Hydrologists, chemists, engineers, and microbiologists need to be involved in these studies so that an adequate interpretation of the results can be made. The processes affecting the movement of ground water and contaminants are complex, and team efforts are generally required in order to design successful experiments, to monitor events, to make proper mass balances on introduced chemicals, and to properly interpret results. In this way, the wrong interpretation of complex results might best be avoided and experimental design is more apt to succeed. The potential for success in stimulating the biological decomposition of a wide range of common ground water contaminants, however, appears very good.

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MICROBIOLOGICAL PARAMETERS CONTROLLING PLUGGING OF WELLS AND GROUNDWATER SYSTEMS

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ABSTRACT

The plugging of well screens and the neighboring interstitial zones of the aquifer can be microbiological in origin. In Saskatchewan, most microbial plugging is a direct result of biofilm generation. Microbiological examination of the wells revealed a diverse group of bacteria involved. These have been differentiated into three groups: (1) *Gallionella*, (2) other bacteria able to deposit iron or manganese oxides or hydroxides in or around the cell, and (3) heterotrophic bacteria able to grow in a biofilm. The major factors which are involved in developing a predictive formula for the risk of plugging are organic carbon, total iron, total manganese, total Kjeldahl nitrogen, pH, temperature and bacterial loading. A Plugging Risk Factor (P.R.F.) is under development.

INTRODUCTION

As North America moves towards a greater reliance on ground water supplies and becomes more concerned with the pollution of that resource, more attention will be paid to the microbiology of the system. Major foci will relate to hygiene/nuisance/amelioriative factors.

To monitor the hygienic aspects of ground water supplies, the coliform test has performed a parallel role to that for surface waters. Dutka (1973) summarized the historical aspects of the application of the coliform test and highlighted some of its weaknesses. In 1979, Craum suggested that: "Almost half the outbreaks (49%) and illnesses (42%) were caused by the use of either untreated or inadequately treated ground water", suggesting that there is a need to upgrade the standards applied to the hygienic quality of ground water sources. Today, more attention is being paid to the risks of other bacteria and viruses penetrating through the ground water systems and causing health problems (Cullimore, 1982).

Interest is also increasing in the control of the nuisance/ameliorative activities of microorganisms in ground water systems. Most well-known of the nuisance roles is the presences of "iron bacteria" causing discoloration, turbidity, plugging and triggering corrosion in wells (Cullimore and McCann, 1978). Ameliorative activities include the utilization of microorganisms within an aquifer formation to degrade potentially harmful chemical compounds (Cullimore, 1984) with or without enhancement.

The major discussion in this paper relates to the role of bacteria during the plugging of wells as a result of the growths of "iron bacteria". Well plugging has been subject to two major reviews (Cullimore & McCann, 1978 and Smith, 1983). The control of plugging by disinfectant has been reviewed (Cullimore, 1980). Physical control techniques have also been reported (Cullimore, 1983).

Plugging usually occurs in a well through biofilm growth constricting the flow of water entering the well through the screen slots and the interstitial zone in the aquifer immediately surrounding the well. The probable reason for this extensive growth at the aquifer/well interface is the increase in oxygen concentration which occurs as a result of the diffusion of oxygen down the water column (Cullimore, 1984). The mechanism of biofilm generation as the critical component in biological plugging has not been extensively studied in the well screen/aquifer environment. Biofilms can however be cultured outside of the natural environment. One such system is the Robbin's biofilm sampler (Microbios Limited, Calgary, Alberta) which was developed to culture biofilms similar to those occurring in heat exchangers and medical equipment where microbial plugging or biofilm growths have generated identifiable problems.

In Saskatchewan, Cullimore and McCann (1978) considered three aspects of plugging to be serious: (1) reduced flow from the wells (sometimes causing a complete shutdown of the system); (2) reducing the quality of the water (through the generation of turbidity, taste, odor and color), and (3) acting as a precursor to the generation of serious anaerobic corrosion problems. The microbiological components involved in plugging has been documented (Cullimore and McCann, 1978, Smith, 1983 and Cullimore, 1984).

The methods for estimating both the chemical and microbiological components are considered in this paper along with considerations for a method to predict plugging in a given well (Plugging Rate Factor, P.R.F.).

MICROBIOLOGICAL ASPECTS OF PLUGGING IN SASKATCHEWAN

The degeneration in well productivity due to plugging has long been a serious financial drain on the province's economy. Estimates place the annual cost at between (Can.) $10 and $12 million. Two major economic costs of plugging relate to: (1) the loss of flow to an extent requiring corrective treatment of the well or abandonment, and (2) the additional treatment required for the poor quality water pumped from the well. This poor quality relates particularly to turbidity, color (generation of yellow to orange to reddish-brown color) and interferences with subsequent treatment systems.

Early studies on the microbiological aspects concentrated on the development of a simple field test kit first reported by Cullimore and McCann (1978). The test method employed a concentrated modified Winogradsky's medium which upon dilution with 15 ml of the sample water upon incubation at room temperature for six days, a brown ring (indicates iron bacteria were present while a black precipitate indicates hydrogen sulfide was present). Concurrently, an MF method for enumerating iron bacteria (long considered to be the major cause of microbial plugging) could be differentiated into three distinctive nutritional groups. Group One: the chemoautotrophic bacteria (i.e. *Gallionella*) common in wells having high iron values (above 1 mg/l) but relatively low concentrations of total organic carbon. Group Two: other "iron bacteria" accumulating ferric and manganic oxides and hydroxides. This group includes *Leptothrix*, *Crenothrix* and *Sphaerotilus* and requires higher levels of total organic carbon. Group Three: heterotrophic bacteria able to grow in the well environment, producing a slimy type of surface growth in which ferric and manganic compounds are deposited. The mixed success using disinfectant therapies (including chlorine and acids) may relate to the different types of slime plugging which can occur in wells (Cullimore, 1980).

Microbiological surveys of wells in Saskatchewan have revealed fluctuations in the populations of iron bacteria and other microorganisms. This would tend to support the hypothesis of Reasoner (1983) that fluctuations in the cell densities were much greater in ground water than in surface waters. Such was the finding of Cullimore (1983a) when examining a major pseudomonad infestation in a well at Shilo, Manitoba. Here, there were intermittent pulses of pseudomonads occurring in the pumped water with numbers reaching as high as 800,000 pseudomonads/ml. The reason for this fluctuation was that while the input of solvents into the aquifer was continuous, the oxygen entered the aquifer through rain precipitation percolating through the very sandy soil. Degradation of the solvent occurred as the oxygenated water approached the well. Consequently, the water was free of hydrocarbons (organoleptically) but high in pseudomonads. Once the dissolved oxygen in the aquifer was consumed (without recharge), then the strictly aerobic pseudomonads were unable to degrade and the hydrocarbons which again appeared and were detected in the well water.

The sporadic success of control measures to reduce microbiological plugging in wells highlights the need for a more complete understanding of the factors which cause plugging in a well. Like the Langellier's and Ryznar's indexes for corrosion/encrustation of wells and the use of calcium hardness to determine softening requirements, there would appear to be a need to determine the potential for microbiological plugging in a given well situation. It could be achieved through an interpretation of physico-chemical and microbiological parameters into a meaningful Plugging Risk Factor (P.R.F.).

AN EVALUATION OF THE POTENTIAL TO DETERMINE THE PLUGGING RISK FACTOR FOR WELLS

Stanier, Dudoroff and Adelberg (1970) proposed the gravimetric formula for microbial forms to be: $C_{50}H_{8}O_{20}N_{14}P_{3}S_{1}Ka_{1}Ca_{0.5}Mg_{0.5}Cl_{0.5}Fe_{0.2}Rest_{0.3}$ could be applied. Some major nutrients can be readily identified as carbon, nitrogen, phosphorus, sulfur, potassium and sodium. In terms of microbial activity, carbon, nitrogen, phosphorus and sulfur have long been considered to be the key nutrients. In wells, the frequent occurrence of high concentrations of iron and manganese in the ferrous and manganous form (eventually to become oxidized to the ferric and manganic forms) also become key factors in the development of plugging where iron bacteria are involved.

For carbon, this may be obtained inorganically in the case of group one iron bacteria, or heterotrophically in the organic form for iron bacteria of groups two and three. If the total organic carbon concentrations are considered to relate directly to the amount of microbial activity which occurs in water (subject to the other environmental factors being adequate). However, Haas, Meyer, Paller, Zapkin and Aulenbach (1983) suggested that total organic carbon did not appear to be a governing factor for microbial growth. The authors postulated that the population appeared to be more associated with low temperature, high dissolved oxygen and turbidity.

Dutka, Walsh, Ewan, El-Shaaravis and Tobin (1983) found a positive link between the presence of *Legionella* in water distribution systems in Central Canada and greater than 0.6 mg/l of particulate organic carbon. Since many of the microorganisms reported in ground water systems preferentially grow in an attached form, the amount of organic carbon present in a particulate form may give a higher correlation to the number of microorganisms present.

Where the concentrations of organic carbon may be low in groundwater, the flow rate into a well could provide a large potentially oxic surface area to generate a microbial biofilm. Biofilm generation and plugging would also be affected by the bio-availability of the organic fraction in the water.

Other nutrients involved in microbial growth have been summarized by Atlas and Bartha (1981). Principal among these nutrients are nitrogen, an essential element in the synthesis of proteins and nucleic acids. In using nitrogen in a predictive formula for microbiological growth, one major difficulty arises in that various groups of microorganisms are able to utilize very diverse sources of nitrogen. In a predictive formula, one of the most difficult predictive areas would be assessing the potential for nitrogen fixation. In the last decade, an increasing number of bacteria have been shown to be able to fix nitrogen.

Most heterotrophic microorganisms are able to utilize ammonia, amino acids, and even (indirectly) nitrates and nitrites as the nitrogen source. For the vast majority, total Kjeldahl nitrogen (including ammonia) represents the most suitable index of available nitrogen for growth and could most be readily employed in a predictive formula.

Kuentzel (1971) considered phosphorus to be the major nutrient influencing algal growth eutrophication. He calculated that in a fresh water system, 1 kg of phosporus would generate 500 kg of algal growth. Sweazy (1970) developed a formula for fresh water systems whereby a state of "biological stability" generates a fixed proportion of the phosphorus fractions present in the system. From this study, it was apparent that four fractions exist. These are soluble inorganic phosphorus (SIP), soluble organic phosphorus (SOP), particulate organic phosphorus (POP) and the particulate inorganic phosphorus (PIP). In a biologically state, a fixed ratio exists between the SIP, SOP, and PIP plus POP (which would include "particulate suspended microbial fraction"). The ratio proposed was 14 ± 5%, 13 ± 3%, and 73 ± 6% respectively. There is relatively little information on the critical concentration of phosphorus in ground water which will initiate growth and support of an expontential growth and storage of phosphorus reserve. For the eutrophic algae, the concentration ranges vary considerably from reference to reference with the lowest critical concentration to support growth documented in the literature ranging from 0.009 to 0.5 mgP/l for minimum concentrations to achieve growth to optimal concentrations occur in the range of 1 to 5 mg P/l (Cullimore, 1973).

Assuming that phosphorus requirements for bacteria were similar to those already established for fresh water algae, then there would appear to be a critical concentration for minimum microbial growth and biofilm generation at between .05 and .1 mgP/l which would have to be incorporated into a predictive formula for biofilm growth and possible plugging.

While much of the attention has been paid to plugging by "iron bacteria", biofilms can be generated without their presence. However, there have been some studies on the relationships of the concentration of iron and manganese in ground water to the generation of a "iron bacterial" type of plugging. Cullimore and McCann (1978) in a literature search found that the iron concentration in water most frequently associated with growth was between .1 and 1 mg Fe/l while for manganese undesirable growths began at between .05 and .15 mg Mn/l. At concentrations of iron and/or manganese above these levels, "iron bacteria" grew readily given that the other physico-chemical factors were not restrictive.

Oxygen, while critical to the growth of the aerobic bacteria, has not been quantified as to the concentrations which will support growth. Provided that oxygen is present in the system, it may not be a major component in any predictive plugging risk formulation.

Temperature has a direct effect on microbial growth and in Saskatchewan where the water temperatures vary from 3 to 12°C, this growth would be psychophilic. There is relatively little hard information available on the interaction of temperature (particularly mild fluctuations) on the growth of iron bacteria. In general, rapid growth could be expected in water systems where the temperature exceeded 7 to 8°C given that other factors were favorable for the growth of psychophilic bacteria. Inadequate data, however, exists for the inclusion of temperature as a major factor in a predictive plugging formulation.

pH has been linked to the growth of iron bacteria and Atlas and Bartha (1981) plotted the iron bacteria as able to grow over an Eh (mV) of +200 to +800 with a pH range of 3 to 7. In attempting to project the type of iron bacteria present in water, there would need to be a differentiation based upon pH from those bacteria favoring an acidotrophic regime such as *Thiobacillus ferrooxidans* and those growing preferentially in mildly alkaline regimes (such as *Crenothrix, Leptothrix* and *Gallionella*). The development of a P.R.F. for wells which can be applied by the analysis of specific physico-chemical microbiological factors in a new well must be developed on the basis of analyzing those parameters that will relate in a direct way to a potential plugging problem. Some components in the development of a P.R.F. would be the concentrations of total iron, total manganese, total phosphorus, total nitrogen, total organic carbon, pH, and a microbial enumeration for iron bacteria, pseudomonas, gross bacteria and coliforms. The weighing of these various factors is presently being developed to form a more complete P.R.F.

A P.R.F. value would be useful in the development of a well treatment program. Preventative maintenance could then be undertaken to restrict the potential growth of these plugging bacteria by either physical or chemical means.

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THE EXTRACTION AND DETERMINATION OF ATP FROM SOIL AND SUBSURFACE MATERIAL

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ABSTRACT

ATP, the living cell's currency of energy, is uniquely suited as an indicator of biomass, i.e., the amount of living material present. The biomass in soil and subsurface material (reflecting biological activity) functions to determine the transport and fate of pollutants.

Firefly luciferase constitutes a sensitive and specific assay for ATP. While the difficulties in extracting ATP from microorganisms in liquid samples have been solved, the extraction of ATP from soil and subsurface material was still a major unsolved problem prior to the research reported in this paper.

The prior state of knowledge concerning the extraction of ATP from soil is reviewed. We developed an extractant mixture composed of H_3PO_4, EDTA, adenosine, urea, DMSO, and Zwittergent 3,10. Each component functions to either eliminate possible interferences or is required to release the ATP. An extraction procedure was also developed. With six different Oklahoma soils we obtained a recovery of 98% of the ATP from added *Escherichia coli* cells. For details and experimental evidence consult our Soil Biology and Biochemistry paper (Webster et al., 1984).

INTRODUCTION

Holm-Hansen and Booth (1966) proposed adenosine 5'-triphosphate (ATP) as a measure of biomass in sea water. ATP measurements were also tested as the basis for a search for extraterrestrial life (MacLeod et al., 1969). An ideal biochemical indicator of living material or a measure of biomass should : 1) be specifically required for biological activity and life, 2) be present in a relatively constant amount per unit of living material, 3) be rapidly degraded or inactivated after cessation of biological activity, 4) be present in measurable amounts in all living material, and 5) be amenable to a sensitive and specific determination. ATP meets these requirements. The most used method for the determination of ATP and the other adenine nucleotides is with firefly luciferase. Leach (1981) has reviewed ATP determination by this method.

Extraction of ATP and/or the other nucleotides from organisms and/or environmental samples requires: 1) rapid quenching of all metabolic reactions and destruction of enzymes that catalyze metabolism of the nucleotides, 2) solubilization of all of the nucleotides present, 3) the absence of material which interferes with solubilization or a means to circumvent such inhibition, 4) either the solubilization of no compound that interferes with the assay or development of a way to circumvent such interference, and 5) a means to monitor the effectiveness of extraction and to determine the efficiency of the assay.

When the environmental sample is a sediment or soil, the extraction of ATP is more difficult than with liquid samples. There may be less ATP present, there may be substances present that interfere with the extraction, and/or there may be substances present that interfere with the luciferase assay. The composition of soils and sediments vary resulting in variations in the conditions required for extraction and possible interfering substances. Most of the extractants used for sediments and soils were originally developed for extraction of ATP from microbial cultures or from liquid samples (Jenkinson and Ladd, 1981).

Table 1 reviews the publications in which two or more extractants have been compared on soils or sediments. The efficiencies of extraction have been calculated and are presented to allow a quantitative comparison.

Table 1. Comparison of Various Extraction Methods for Soils and Sediments

Author	Reference	Extractant	Relative effectiveness
Ausmus	(1973)	1-Butanol	1
		0.6 $\underline{M}$ H_2SO_4 *	1
		90 % DMSO, 0.05 $\underline{M}$ Tris	0.56
		0.4 $\underline{M}$ $HClO_4$	0.48
		0.02 $\underline{M}$ Tris pH 7.75, boil	0.47
		90 % DMSO, 0.1 $\underline{M}$ H_2SO_4	0.39
		0.01 $\underline{M}$ $\underline{n}$-Bromosuccinimide, 0.01 $\underline{M}$ EDTA, 0.02 $\underline{M}$ K_2HAsO_4 pH 7.4	0.37
Bancroft, Paul, & Wiebe	(1976)	0.6 $\underline{M}$ H_2SO_4	1.0
		0.1 $\underline{M}$ $NaHCO_3$ pH 8.5, boil*	1.0
		0.02 $\underline{M}$ Tris pH 7.8, boil	0.8
		50 % 1-Butanol, 50 % 1-Octanol	0.8
		0.4 $\underline{M}$ $HClO_4$	0.8
Bulleid	(1978)	0.04 $\underline{M}$ Na_2PO_4, Citrate pH 7.7*	1.0
		0.065 $\underline{M}$ Phosphate buffer pH 7.7	0.89
		0.1 $\underline{M}$ $NaHCO_3$ pH 8.3	0.54
		0.02 $\underline{M}$ Tris pH 7.7	0.17
Christensen & Devol	(1980)	1.2 % v/v Triton X-100, 0.75 $\underline{M}$ H_3PO_4, 0.075 $\underline{M}$ H_2SO_4*	1.0
		0.6 $\underline{M}$ H_2SO_4	0.2
Conklin & MacGregor	(1972)	25 % 1-Butanol, 0.015 $\underline{M}$ Arsenate, 1-Octanol, 0.015 $\underline{M}$ EDTA pH 7.5*	1.0
		0.02 $\underline{M}$ Tris pH 7.75	0.19
		0.01 $\underline{M}$ $\underline{N}$-Bromosuccinimide, 0.01 $\underline{M}$ EDTA, 0.02 $\underline{M}$ K_2HAsO_4 pH 7.4	0.02
		0.23 $\underline{M}$ HCOOH, 0.001 $\underline{M}$ EDTA	0.01
Cunningham & Wetzel	(1978)	1.1 $\underline{M}$ H_2SO_4, 0.063 $\underline{M}$ Oxalic acid*	1.0
		0.6 $\underline{M}$ H_2SO_4,	0.77
		0.1 $\underline{M}$ $NaHCO_3$, boil pH 8.5	0.54
		0.025 $\underline{M}$ HEPES after freezing	0.50
		0.025 $\underline{M}$ HEPES pH 7.5, boil	0.08
		0.6 $\underline{M}$ H_2SO_4, 0.048 $\underline{M}$ EDTA	0.08
Eiland	(1979)	1.5 $\underline{M}$ H_2SO_4*	1.0
		90 % DMSO in 0.1 $\underline{M}$ H_2SO_4	0.98
		0.02 $\underline{M}$ Tris	0.91
		1.5 $\underline{M}$ Trichloroacetic acid (TCA)	0.48
		1.5 $\underline{M}$ $HClO_4$	0.31
Hodson, Holm-Hansen, & Azam	(1976)	0.6 $\underline{M}$ H_2SO_4, charcoal column*	1
		0.6 $\underline{M}$ H_2SO_4	0.17
		0.02 $\underline{M}$ Tris pH 7.8, boil	0.04
Jenkinson & Oades	(1979)	0.5 $\underline{M}$ TCA, 0.25 $\underline{M}$ Na_2HPO_4, 0.1 $\underline{M}$ Paraquat*	1
		0.5 $\underline{M}$ TCA, 0.25 $\underline{M}$ Na_2HPO_4	0.62
		0.5 $\underline{M}$ TCA	0.12
		0.6 $\underline{M}$ H_2SO_4	0.10
Karl & Craven	(1980)	1 $\underline{M}$ H_3PO_4, 0.048 $\underline{M}$ EDTA*	1
		0.065 $\underline{M}$ Phosphate pH 7.7	0.81
		0.6 $\underline{M}$ H_2SO_4, 0.048 $\underline{M}$ EDTA	0.09
Lee, Harris, Williams, Armstrong, & Syers	(1971)	0.6 $\underline{M}$ H_2SO_4*	1

(continued)

	90 % DMSO, 0.1 M H_2SO_4	0.53
	0.6 M $HClO_4$	0.53
	90 % DMSO, 0.05 M Tris	0.11
	0.01 M N-Bromosuccinimide	0.10
	0.02 M Tris pH 7.75, boil	0.10
Tobin, Ryan & Afghan (1978)	0.008 M Na_3PO_4, 33 % $CHCl_3$*	1
	0.06 M H_2SO_4, charcoal	0.16
	0.6 M H_2SO_4, ion exchange	0.14

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* The extractant of choice. The extractant with the greatest effectiveness in each set was taken as 1 and each of the other extractants used in direct comparison is expressed as a fraction of that effectiveness. The recovery of ATP or the maximum amount of ATP from the soil or sediment was used as a measure of relative effectiveness.

This paper reports the development of an extraction mixture to minimize the effects of the various interferences which might occur. The extractant mixture contains H_3PO_4, EDTA, adenosine, urea, DMSO, and Zwittergent 3,10. The phosphoric acid provides acid for extraction and inactivation of proteins, and phosphate to saturate phosphate binding sites and to complex and/or precipitate metal ions. The EDTA chelates metal ions, prevents inhibition of luciferase, and aids in lysis of the bacterial cells. The adenosine serves to saturate the ATP binding sites which could act by either hydrogen bonding or by base stacking interactions. Urea denatures protein (inactivates enzymes) and prevents hydrogen bonding. DMSO removes cells from surfaces and lyses them. Zwittergent 3,10, which is not irreversibly bound to either anionic or cationic compounds, is used below its critical micellar concentration to remove bacterial cells from surfaces and to lyse them. Polytron treatment is used to remove bacteria from surfaces, insure adequate mixing, and help disrupt cells. This extractant was applied to soil samples varying widely in their properties. An internal standard of *Escherichia coli* cells was used to determine the efficiency of extraction and assay.

MATERIALS AND METHODS

The assays and materials used have been described by Webster and Leach (1980). The soils used and the extraction procedure have been described by Webster et al. (1984). The other extractions were according to the cited reference.

RESULTS

The optimum concentration of each of the components of the extractant was determined (see Webster et al., 1984). We also tried various alternative formulations of the extractant (different concentrations and omissions) with various soils, but we found that the described extractant was the best. We recovered an average of 98% of the ATP from *E. coli* added to soil samples.

When compared to the best extractants in the literature, the newly formulated extractant and procedure proved superior (see Table 2). The recovery of ATP from added *E. coli* cells was greatest with our procedure and the amount of ATP obtained from a soil sample was also greatest with our extractant.

Table 2. Comparison of Various Extraction Mixtures with the Complete Extraction Mixture

Extractant	Reference	Recovery of *E. coli* ATP %	ATP Content of Webster soil ng/g
A. Boiling			
0.1 M $NaHCO_3$	Bancroft, Paul & Wiebe (1976)	75	189
Na_2HPO_4 + citrate	Bulleid (1978)	48	28
0.02 M Tris	Levin, Schrot & Hess (1975)	72	102
B. Room temperature			
90% butanol	Sharpe, Woodrow, & Jackson (1970) modified	51	306
Butanol + octanol + arsenate + EDTA	Conkin & MacGregor (1972)	68	75
90% DMSO + 0.1 M H_2SO_4	Lee, Harris, Williams, Armstrong & Syers (1971)	69	330
Na_3PO_4 + $CHCl_3$	Tobin, Ryan & Afghan (1978)	61	154
C. 4°C			
1.5 M H_2SO_4	Eiland (1979)	43	17
H_2SO_4 + oxalic	Cunningham & Wetzel (1978)	73	68
Triton + H_3PO_4 + H_2SO_4	Christensen & Devol (1980)	83	86
H_3PO_4 + EDTA	Karl & Craven (1983)	57	46
TCA + Na_2HPO_4 + paraquat	Jenkinson & Oades (1980)	85	47
H_3PO_4 + adenosine + urea + EDTA + DMSO + Z 3,10	This paper	97	343

The procedure described in the Materials and Methods section was applied to a sample of Webster soil and then the ATP content of the extract was determined by our standard assay as is described in the Materials and Methods section. For the 90 % 1-butanol a 1 g sample of soil was incubated at room temperature for 10 min and centrifuged.

DISCUSSION

The criteria selected for the evaluation of the effectiveness of various extraction procedures were 1) the amount of ATP as assayed by the firefly luciferase reaction extracted from a standard soil sample, 2) the recovery of ATP from a sample of *E. coli* cells added to the soil prior to extraction, 3) the effect of the extraction mixture on solubilizing inhibitors that might interfere with the assay of ATP, and 4) these same effects measured on a variety of soils that represent the soil types that occur in Oklahoma. We found every component of the mixture essential with at least one soil or reduced variability. We used dilution to overcome inhibition in the assay. Others used charcoal (Hodson et al., 1976) or ion exchange resins (Eiland, 1979) for the purification of the extracted ATP. We found these procedures time consuming and tedious.

ACKNOWLEDGMENTS

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MICROBIAL REMOVAL OF TRACE ORGANICS DURING RAPID INFILTRATION RECHARGE OF GROUND WATER

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ABSTRACT

Soil column tests and field experiments were designed to evaluate microbial removal of trace organics during rapid infiltration recharge of ground water. Column tests using acclimated soil from an operational system demonstrated good removal of trace organics. Increased concentrations of target compounds in the feed did not always result in corresponding increases in the column effluent. Microbial adaptation was evident for some compounds. Other compounds appeared to exhibit a minimum concentration below which biodegradation did not proceed. Microbial activity was confirmed as a fate mechanism for several target compounds using radiolabels. In direct correlation with field results, the induction of anaerobiosis in the soil columns resulted in increased fractional breakthrough of trace organics.

INTRODUCTION

Land application is generally effective for the removal of many wastewater constituents such as fecal coliforms, heavy metals, phosphorus, and carbonaceous biochemical oxygen demand (Bouwer and Chaney, 1974; Iskandar, 1978; Olson et al., 1980). There have been few comparable studies on trace organic fate in land application systems. This is of particular concern in rapid infiltration systems because, unlike other land application practices, rapid infiltration depends primarily on percolation for wastewater disposal and thus has the greatest potential for affecting associated ground waters (Environmental Protection Agency, 1977).

A survey of several rapid infiltration sites in the U. S. has demonstrated that many wastewater trace organics are completely or mostly removed by the treatment process although detectable concentrations of recalcitrant compounds are still present in the associated ground waters (Tomson *et al.*, 1984). Other research using soil columns has indicated that biodegradation may be partially responsible for this removal (Bower *et al.*, 1981). We therefore evaluated trace organic transport and fate using soil columns in a series of tests designed to address the effects of microbial involvement in trace organic removal. Because it is not possible to present the complete results in the text of this short paper, additional information can be found in the publications which are referenced in the sections pertinent to the individual test.

MATERIALS AND METHODS

Field Study

A field study was conducted to evaluate trace organic removal at an operational site (Hutchins *et al.*, 1984a). Ground water from a 40-yr-old rapid infiltration facility at Fort Devens, Massachusetts was sampled for trace organic contamination. Three Teflon monitoring wells were installed at a depth of 1.2 m in one of the basins at the site prior to flooding. Flooding was initiated and samples of the raw wastewater, the wastewater entering the basin, the infiltrate at 1.2-m depth, and the ground water down-gradient of the site were obtained continuously over the 6-d flooding period. Sample streams were pumped through XAD-4 resin columns and the columns were replaced every two days. Resin extracts in this study and in the column tests were analyzed for six selected wastewater organics: p-dichlorobenzene (PDCB), 2-methylnaphthalene (2MN), o-phenylphenol (OPP), p-(1,1,3,3-tetramethylbutyl)phenol (TMBP), 2-(methylthio)benzothiazole (2MTBT), and benzophenone (BZPN).

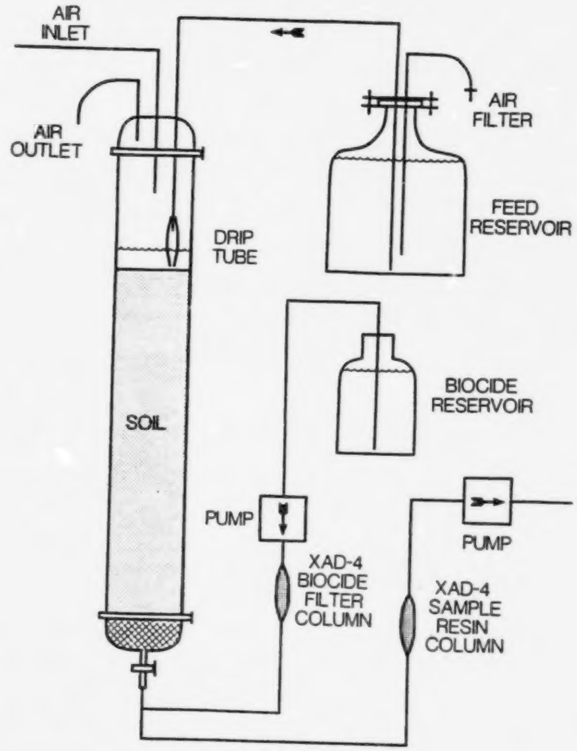

Fig. 1. Column design schematic.

Column Test System

The soil columns and associated plumbing were constructed of Teflon and glass to minimize adsorption and leaching of trace organics (Fig. 1). The columns received feed solution from reservoirs equipped with Mariotte siphons to maintain a constant level of feed above the soil. After a flooding period ended, the siphon was disconnected and the columns drained until the next flooding period began. A proportioning pump was connected to the column effluent line for controlling infiltration rates. Feed solutions and column effluents were analyzed for trace organics using Amberlite XAD-4 resin and gas chromatography/mass spectrometry as described elsewhere (Hutchins *et al.*, 1983). One resin column was used to adsorb trace organics from each soil column effluent during the entire flooding period of a single inundation cycle. An identical analysis was performed on the feed solution so that fractional breakthroughs (mass output/mass input) of each compound could be calculated. Concentrations of each compound were estimated based on the mass eluted from the resin and the volume sampled. Biocide was added to the sample stream prior to contact with the resin so that biodegradation of sorbed trace organics would be inhibited during sampling.

Column Test

The column test was designed to evaluate microbial removal of wastewater organics as a function of input concentration for an operational system and to compare trace organic mineralization in acclimated and nonacclimated soil (Hutchins *et al.*, 1984b). Subsequent to the field study, soil was obtained from the Fort Devens site and packed into eight columns. Primary wastewater was separated into four aliquots, and each aliquot was amended with the six wastewater organics evaluated in the field study so that the aliquots yielded final concentrations of approximately 1, 10, 100, and 1000µg/l of each compound. Each set of duplicate soil columns received feed from one of the aliquots on a 6-d flooding/16-d drying cycle at an average infiltration rate of 1.4 cm/hr. After the third inundation cycle, one of the soil columns which had received the compounds at 10µg/l concentration was dismantled. Soil samples from this column and from a site adjacent to the basins at Fort Devens were used to test for mineralization of radiolabeled compounds.

The soil columns were then modified so that anaerobic conditions could develop during flooding (Hutchins *et al.*, 1984c). Each column was initially flooded with unfiltered primary wastewater for six days to deplete the residual oxygen in the system. After the system became anaerobic, feed solutions were prepared and the columns were operated anaerobically for an additional 6-d flooding period.

RESULTS

Field Study

Results from the field study demonstrated that most of the removal occurred in the top meter of the basin during infiltration. This removal was consistent for all six selected compounds during the first two days of the flooding period; basin infiltrate concentrations were generally an order of magnitude lower than floodwater concentrations (Table 1). However, basin infiltrate concentrations of all six compounds began to increase at two of the sample points as flooding continued (Table 2). Concentrations of PDCB, 2MTBT, TMBP, and BZPN in the basin infiltrate at one of the sample points exceeded floodwater concentrations during the final two days of flooding.

Table 1. Trace organic data for raw sewage (duplicate), basin floodwater (triplicate), and basin infiltrate (triplicate) samples during first two days of flooding period (Hutchins et al., 1984a).

Trace Organic	Raw Sewage	Basin Floodwater	Basin Infiltrate
		µg/l	
PDCB	0.67 ± 0.10[a]	0.32 ± 0.11	0.044 ± 0.013
2MN	0.33 ± 0.01	0.22 ± 0.07	0.012 ± 0.015
OPP	0.93 ± 0.06	0.43 ± 0.17	0.037 ± 0.037
TMBP	0.79 ± 0.11	0.44 ± 0.22	0.17 ± 0.07
2MTBT	0.39 ± 0.01	0.59 ± 0.27	0.091 ± 0.025
BZPN	0.73 ± 0.44	0.40 ± 0.29	0.040 ± 0.026

[a] Mean ± standard deviation

Table 2. Trace organic data for raw sewage (duplicate), basin floodwater (triplicate), and basin infiltrate (triplicate) samples during final two days of flooding period.

Trace Organic	Raw Sewage	Basin Floodwater	Basin Infiltrate		
			Well #1	Well #2	Well #3
			µg/l		
PDCB	0.92 ± 0.14[a]	0.43 ± 0.29	0.033	0.20	0.60
2MN	0.30 ± 0.06	0.27 ± 0.02	0.014	0.019	0.23
OPP	0.82 ± 0.08	0.92 ± 0.19	0.032	0.47	0.87
TMBP	0.56 ± 0.01	0.75 ± 0.34	0.15	0.29	1.1
2MTBT	0.33 ± 0.02	0.69 ± 0.31	0.084	0.47	0.96
BZPN	0.44 ± 0.41	0.33 ± 0.08	0.20	0.41	0.88

[a] Mean ± standard deviation

Column Test

The relationship between feed concentration and column effluent concentration was different for virtually each compound studied. Breakthrough profiles for OPP were consistent during the test with column effluent concentrations increasing proportionately with input concentrations, i.e., fractional breakthrough was constant (Fig. 2a).

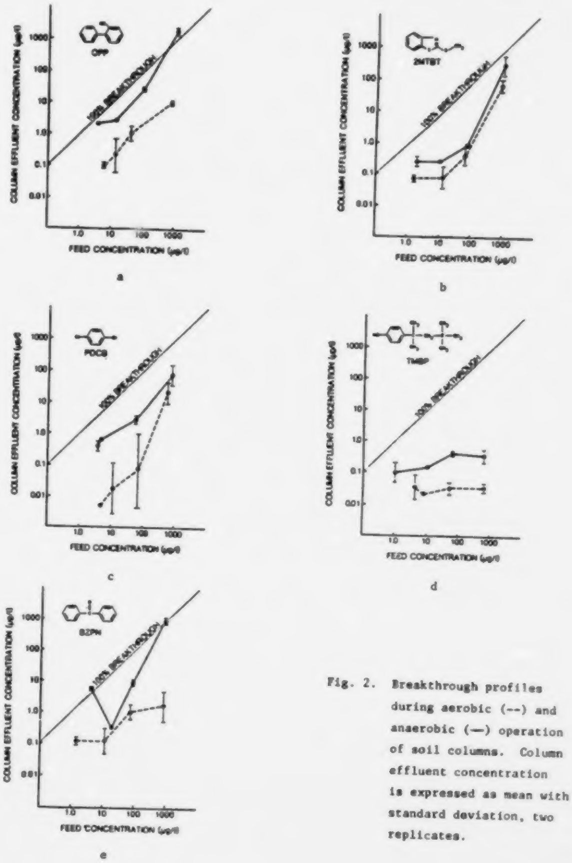

Fig. 2. Breakthrough profiles during aerobic (--) and anaerobic (—) operation of soil columns. Column effluent concentration is expressed as mean with standard deviation, two replicates.

Consistent profiles were also observed for 2MTBT although fractional breakthroughs were higher at lower input concentrations (Fig. 2b). The behavior of PDCB was similar to that of 2MTBT after the first inundation cycle with the exception that increased fractional breakthroughs were observed at the highest input concentration as well (Fig. 2c).

Microbial adaptation was evident for BZPN, TMBP, and 2MN as indicated by increasing removal efficiencies during successive inundation cycles, especially at the higher input concentrations (Unpublished data). Column effluent concentrations of 2MN were independent of feed concentrations during the second inundation cycle, and 2MN could not be detected in any of the column effluents afterwards. Similarly, column effluent concentrations of TMBP stabilized during the third inundation cycle (Fig. 2d), and the data for BZPN indicated that a similar trend might occur with time (Fig. 2e). No significant mineralization of PDCB, TMBP, and 2MTBT occurred in the nonacclimated forest soil from the site, whereas mineralization of the compounds in the column soil ranged from 0.4 to 20% of the theoretical input for 2MTBT and OPP respectively during the 16-hr incubation (Table 3). With the exception of BZPN, each compound was more rapidly mineralized in the acclimated soil than in the nonacclimated forest soil. Rates of removal were 20 to 1000 times faster than rates of mineralization for OPP and 2MTBT respectively.

Table 3. Mineralization of test compounds in acclimated soil from one of the columns used in the third column test and in non-acclimated forest soil (Hutchins et al., 1984b).

Soil Sample	CO_2 Evolved (% of Theoretical ± Standard Deviation)[a]					
	PDCB	2MN	OPP	TMBP	2MTBT	BZPN
Forest Soil and Biocide	0.75 ± 0.09 [b]	0.86 ± 0.05	0.29 ± 0.03	0.57 ± 0.25	0.16 ± 0.10	0.47 ± 0.13
Forest Soil	0.72 ± 0.08	6.18 ± 2.24	1.36 ± 0.18	0.86 ± 0.55	0.27 ± 0.11	1.78 ± 0.17
Column Soil and Biocide	2.63 ± 0.06	0.64 ± 0.08	0.24 ± 0.02	0.66 ± 0.12	0.14 ± 0.08	0.45 ± 0.13
Column Soil	6.52 ± 0.63	16.3 ± 3.0	20.7 ± 1.2	7.0 ± 1.9	0.58 ± 0.15	2.38 ± 0.55

[a] Three samples

[b] Brackets indicate that the difference between the values is not significant at the 95 percent confidence level.

Fractional breakthrough profiles for OPP, 2MTBT, and TMBP did not change when the soil became anaerobic, although the degree of breakthrough increased for each compound compared to aerobic operation (Figs. 2a, 2b, 2d). Anaerobic conditions also promoted increased fractional breakthrough of PDCB, although the effect was most pronounced at the lower input concentrations (Fig. 2c). For BZPN, the effect was most pronounced at both the lowest and highest input concentrations (Fig. 2e). In contrast, 2MN could not be detected in the column effluent during either aerobic or anaerobic operation. Leaching was evident for OPP and BZPN, because effluent concentrations from some of the columns were higher than feed concentrations.

DISCUSSION

Microbial activity was evaluated in the third column test by examining the effect of concentration of the compound on its removal during infiltration. For all input concentrations tested, the concentration of the compound in the column effluent was proportional to input concentration only for OPP. The removal of OPP is therefore first-order in kinetics and the removal rate constant is independent of the initial concentration. Because several abiotic removal processes in nature are firstorder, the breakthrough profile of OPP is not necessarily an indication that microbial activity is involved. Evidence of this is given by the occurrence of mineralization during the isotope study. For the other compounds, however, evidence of microbial activity is also given by the shape of the breakthrough profiles because removal processes are shown to be less efficient at lower concentrations. Low concentrations do not impose constraints on abiotic first-order removal processes; the data therefore suggest that biotic mechanisms may be involved. This observation is consistent with the concept of a minimum substrate concentration (McCarty *et al.*, 1981), which states that a threshold concentration of a substrate can exist below which no further biodegradation occurs. This concept was developed from the study of biofilms and is applicable only to the metabolism of a primary substrate. Concentrations of the test compounds were relatively minor compared to the total organic carbon content of the wastewater which should presumably serve as sources of primary substrates. The lack of significant mineralization observed for PDCB, BZPN, and 2MTBT indicates that these compounds are probably not being used as primary substrates by the soil microorganisms. If these compounds are being transformed via cometabolic pathways, no threshold concentration should theoretically exist (Bouwer and McCarty, 1983). The fact that threshold concentrations were observed for 2MTBT and BZPN indicates that these theoretical considerations are insufficient to explain their fate in soil. Other factors may exist which could result in either a concentration limit for the removal of the compound or in a controlled release of the compound into the column effluent, although the nature of these other factors is unknown.

Trace organic removal during the field study was comparable to that observed in the column test for the soil columns receiving low concentrations of the compounds (Table 1). However, removals were consistent in the column test whereas they began to decline in the field study for two of the sample points towards the end of the flooding period (Table 2). It was hypothesized that this decline was the result of anaerobic conditions which developed with flooding, and this hypothesis was tested during the column test. With the exception of 2MN, fractional breakthroughs of each compound increased when the soil columns became anaerobic (Figs. 2-6). Anaerobic conditions generally increase an organic compound's recalcitrance to biological attack (Alexander, 1965). This is especially true for aromatic compounds. Although some aromatics can be degraded or transformed even under strict anaerobic conditions, these compounds generally require the presence of an oxygenated substituent group for this to occur (Rose, 1976, Healy and Young, 1979; Horowitz *et al.*, 1983). Phenolic compounds would therefore be expected to be somewhat labile under anaerobic conditions (Bakker, 1977; Ehrlich *et al.*, 1982); whether or not this occurs with OPP and TMBP in this system is unknown. It is also difficult to assess the role of anaerobic biodegradation in the fate of 2MN, 2MTBT, and BZPN because of the lack of data for these classes of compounds. In agreement with the data for PDCB, however, other researchers have observed marked decreases in rates of mineralization and biotransformation for halogenated benzenes under anaerobic conditions (Marinucci and Bartha, 1979; Schwarzenbach *et al.*, 1983).

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DENITRIFICATION DURING WASTEWATER RENOVATION GROUNDWATER RECHARGE

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ABSTRACT

Ground water recharge is an effective way to renovate sewage water but recharge systems must be carefully designed and managed to avoid ground water contamination and to produce reclaimed water suitable for reuse. Nitrate can be removed from wastewater by alternating wetting and drying cycles in flooding basins to promote nitrification during the dry periods and denitrification during subsequent flooding periods. The proportion of nitrogen removed by denitrification depends upon the carbon content of the sewage water and the infiltration rate of the recharge basins. Most of the nitrogen can be removed by denitrification from wastewaters with low carbon concentrations like secondary sewage effluent if the infiltration rate is maintained below 15-20 cm/day. Infiltration rates can be controlled by initial site selection, reducing the water depth in flooding basins, changing the suspended solids content of the waste water or by compacting the soil surface.

Denitrification at higher infiltration rates can be increased by increasing the organic carbon content of the wastewater. Soil column studies showed that most of the nitrogen was removed by adding glucose to secondary sewage effluent continuously and denitrification could be substantially increased by adding a pulse of glucose at the beginning of each flooding period. One practical way to increase denitrification is to apply primary sewage effluent rather than secondary effluent. Another practical way to provide additional carbon for increased nitrogen removal from secondary sewage effluent is to mix sewage sludge with the surface few inches of soil.

Ground water recharge is an effective way to renovate sewage water but recharge systems must be carefully designed and managed to avoid ground water contamination and to produce reclaimed water suitable for reuse. Nitrate-N is a key pollutant which can be removed from wastewater by alternating wetting and drying cycles in flooding basins to promite nitrification during the dry periods and denitrification during subsequent flooding periods.

Field studies where groundwater recharge basins were intermittently flooded with secondary sewage effluent showed that systems with high infiltration rates (30 to 60 cm/day) removed most of the fecal microorganisms, organic material, and phosphates (Bouwer et al., 1974). Soil columns were constructed in the laboratory so that all of the water and gases entering and leaving the columns could be measured and sampled. (Lance and Whisler, 1972). Patterns of nitrate peaks and other parameters that could be measured in both the laboratory and the field were quite similar, indicating that the columns were good models of the field system.

Initial laboratory experiments showed that the NH$_4$-N was adsorbed by the soil exchange complex during one flooding period and held until the dry period when oxygen entered the soil and nitrification occurred. The nitrate formed during the dry period was leached from the soil during the next flooding period, and the incoming sewage water provided organic carbon for some denitrification, while the NH$_4$-N of the sewage water was adsorbed at the same time. The difficulty with this approach has been that nitrate which formed during the dry period is leached through the soil in a concentrated peak, and the concentration of organic carbon in the sewage water is too low for complete denitrification. Thirty per cent of the nitrogen was removed when the loamy sand columns were flooded with secondary sewage effluent at infiltration rates of 30 to 40 cm/day (Lance and Whisler, 1972) which agrees well with estimates of nitrogen removed by field recharge basins (Bouwer et al., 1974) at comparable loading rates.

After denitrification was shown to be the only reaction capable of removing the tremendous nitrogen load (25,000 kg/ha/yr) applied in these high-rate systems, the columns were used to determine what factors limited denitrification in soils intermittently flooded with sewage water. A series of experiments with the soil columns then produced techniques to stimulate denitrification and increase nitrogen removal.

PROCEDURE

Soil columns were constructed by packing the loamy sand from basins used for rapid infiltration of secondary sewage effluent into polyvinyl chloride (PVC) pipes. These basins were in the dry Salt River bed near Phoenix, Arizona. Each column was a 2.75-m length of 10-cm (I.D.) PVC pipe filled with 6 cm of pea gravel at the bottom and 250 cm of loamy sand on top. Air-dried soil containing 3% clay, 8% silt, and 89% sand was packed so that bulk densities for each column ranged from 1.5 to 1.7 g/cm^3. A schedule of 9 days flooding with secondary sewage effluent alternated with 5 days drying was used. Sewage water was applied with a Mariotte siphon to maintain a 15-cm constant pressure head at the soil surface. The flow rate and cumulative flow through the columns were measured by weighing the outflow daily, and the cumulative outflow periodically.

In experiments on factors affecting denitrification, four levels of organic carbon were maintained by flooding two columns with secondary sewage effluent and three sets of two columns each with different levels of organic carbon (50, 150 and 200 ppm) added to the sewage water. Later, sewage enriched with 100 to 200 ppm C was added to several columns only during the first 3 days of the flooding period to provide a pulse of carbon moving through the soil. Soil columns flooded with secondary effluent were then operated at various infiltration rates (15 to 45 cm/day) by packing the soil to different densities.

In recycling experiments, water with nitrate concentrations between 20 and 100 ppm was collected from the columns during the second and third day of flooding and mixed with sewage water at the rate of two parts sewage to one part high-nitrate water. The mixture was recharged through the columns during the remainder of the 9 day flooding period.

Similar columns were constructed and placed in an insulated building with the top of the columns protruding through the roof. These columns were used initially to determine the effect of plants on denitrification during flooding with secondary sewage effluent. Common Bermuda grass (*Cynodon dactylon*) was planted in three columns, and three columns remained bare. The same columns were then used to study denitrification during flooding with primary sewage effluent taken from the primary clarifier outlet at the 23rd Avenue wastewater treatment plant in Phoenix, Ariz.

Finally 3 of the laboratory soil columns were used to test the effect of adding sewage sludge to the soil to stimulate denitrification in columns flooded with secondary sewage effluent. Dry sludge was mixed in the top 5 cm of two columns at an application rate equivalent to 50 mt/ha. Infiltration rates of the two columns were 30 and 60 cm/day. Sludge was added to another soil column at the rate of 200 mt/ha and the infiltration was 75 cm/day.

During all experiments, the wastewater and water drained from the columns were sampled daily and analyzed for NO$_2$-N, NO$_3$-N, NH$_4$-N, and PO$_4$-P with a continuous-flow analytical system, and for organic carbon with a total organic carbon analyzer.

RESULTS AND DISCUSSION

Carbon addition experiments.

Nitrogen removal by the soil columns was increased to about 60% by adding enough dextrose to increase the carbon concentration entering the columns to 80 ppm, and to 90% when the carbon concentration was increased to 150 ppm (Lance and Whisler, 1976). The stoichiometric equation for denitrification indicated that 1.3 mg of dextrose-C was needed for every milligram of NO_3-N denitrified. The 150-ppm C concentration was about five times the average N content of the incoming sewage water. High concentrations of organic carbon were needed for complete denitrification in the soil columns because nitrate concentrations in the high-nitrate peak reached 75 to 100 ppm. The 150-ppm C concentration in the dextrose-amended sewage water increased the carbon to nitrate ratio enough to eliminate the nitrate peak. However, the high concentration of carbon was needed only when the nitrate peak passed through the columns. Thus, much of the carbon moved through the column.

In an attempt to supply a pulse of carbon to coincide with the leaching of the nitrate peak through the soil, the carbon concentration of the secondary sewage effluent was increased only during the first 3 days of flooding. The addition of 100 ppm dextrose-C to the sewage increased N removal by 21% at each infiltration rate (Lance and Gilbert 1976) N removal was increased by 33% when 200 ppm carbon was added. Thus, adding carbon as a pulse stimulated denitrification, but did not eliminate the nitrate peak at the higher infiltration rates as did adding 200 ppm carbon continuously. When the C pulse was applied to short columns during only the first 2 days of flooding, the populations of denitrifying bacteria were increased during each flooding period, but they decreased during the drying period to populations similar to those in columns receiving only secondary effluent (Gilbert et al., 1979). Bacterial populations remained high throughout the flooding cycles when carbon was added continuously to the sewage water. Thus populations trends were correlated with nitrogen removal rates.

Methods to mix the nitrate peak with sewage.

Since the addition of dextrose or some other organic carbon source is expensive, it is desirable to utilize the organic carbon of the sewage water to support denitrification. The nitrate peak moving through the soil must be mixed with a large volume of the incoming sewage water to provide sufficient carbon for complete denitrification. One way to provide this mixing was to adjust the infiltration rate so that nitrate was mixed with sewage inside the soil columns (Lance et al.1976). Infiltration rates were varied between 15 and 60 cm/day by packing the columns to different bulk densities. The percentage of nitrogen removal increased exponentially as the infiltration rate decreased (Fig. 1). About 80% of the nitrogen was removed at 15 cm/day infiltration rate. The change in infiltration rate affected nitrogen removal by changing the flow characteristics of the system. Nitrate formed in the soil during the dry period was leached as a narrow concentrated band when the infiltration rate was high. A decrease in infiltration rate caused the nitrate to be leached in a more diffuse wave, allowing considerably more mixing of the nitrate with the infiltrating sewage water. Mixing the nitrate with the incoming sewage water provided a more favorable C to nitrate ratio for denitrification than that obtained when nitrate was leached in a concentrated band. Salt tracer studies confirmed that the amount of mixing depended upon the infiltration rate. A definite relationship between infiltration rate and nitrogen removal probably exists for all soils, but it may be different for each soil. Some methods for changing infiltration rates are adjusting the depth of ponding, compacting the soil surface, and adjusting the suspended solids content of the sewage water.

Reducing infiltration rates to increase nitrogen removal by a rapid-infiltration system was field tested at the Flushing Meadows project in the Salt River bed near Phoenix, Arizona (Bouwer et al., 1980). Approximately 30 percent of the applied nitrogen was removed at a hydraulic loading rate of about 120 m/year. The hydraulic loading rate was reduced to an average of about 65 m/year (during a three-year period) by reducing the ponding depth in the infiltration basins from 30 to 15 cm/day and adjusting the flooding and drying cycles to insure complete nitrification of the applied NH_4-N. These management changes increased the nitrogen removal to about 65 percent and the total nitrogen content of the renovated water was reduced to 9.6 mg/liter.

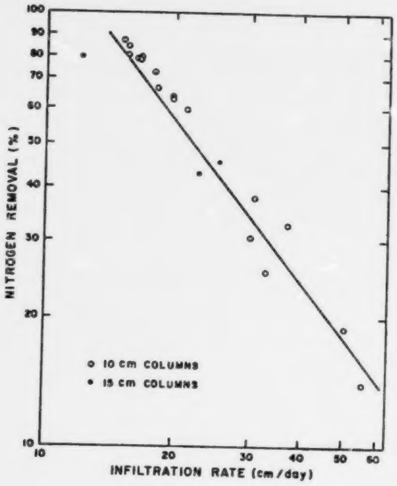

Figure 1. The effect of infiltration rate on nitrogen removal from sewage water by flooded soil columns.

Another way to mix the nitrate peak with the sewage water was to collect the high nitrate water, mix it with two parts of sewage water, and recycle it through the columns. Nitrogen removal ranged from 75-80% when 20-25% of the total volume of water draining from columns with infiltration rates of 25 to 30 cm/day was recycled (Lance et al., 1976). It may be possible to use this method with a land filtration system equipped with tile drains for collecting high nitrate water and a holding pond for mixing it with sewage water, but the method has not been field-tested.

The effect of plants on denitrification.

When soil columns with actively growing grass were flooded with sewage, N removed increased by 10 to 18.5% over that removed by bare soil columns (Lance et al., 1978). The increase in N removal was a result of plant uptake rather than stimulation of denitrification. Clipping the grass and placing it on the soil surface was also ineffective in stimulating denitrification. These results indicated that vegetation can be used with some high-rate land filtration systems to increase N removal from a marginal to an acceptable level. However, growing plants would not be expected to increase N removal in a groundwater recharge system like the Flushing Meadows project (45 cm/day infiltration rate) from the 30% level to above 50%.

Denitrification in soils flooded with primary sewage effluent.

N removal from the three bare soils columns averaged 45.6% for primary effluent as compared with 28.5% N removal from the secondary effluent (Lance et al., 1980). N removal increased because the primary effluent contained more dissolved organic carbon, and thus supported more denitrification. The average dissolved organic carbon concentration in primary effluent entering the columns was about 75 ppm. Previous laboratory experiments in which dextrose was added to secondary sewage effluent described above indicated that increasing the organic carbon content to 75 ppm would increase N removal but would not allow complete denitrification (Figure 2). The data from the primary effluent experiment supported that concept. The experiments suggested that N removal percentages would have been higher from a primary effluent with a higher carbon to nitrogen ratio that the 3:1 ratio found in the primary effluent used. N removals of about 90% were reported for the Hollister, Calif., land filtration site where the C:N ratio of primary effluent was 6:1(Levine et al., 1978). Field tests using small infiltration basins supported the concept that primary sewage effluent could be applied to ground water recharge systems to increase nitrogen removal and reduce in-plant treatment costs (Rice and Bouwer, 1984).

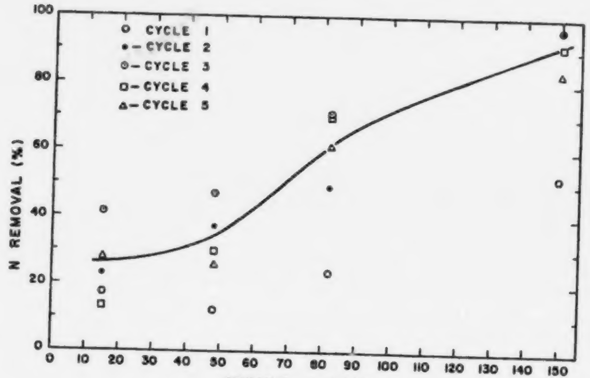

Figure 2: The effect of the organic carbon content of sewage water on nitrogen removal by flooded soil columns.

The effect of buried sewage sludge on denitrification in soil columns flooded with secondary sewage effluent.

Nitrogen removal by the column flooded with secondary sewage effluent at an infiltration rate of 30 cm/day was increased from about 25% to about 55% by incorporating dried sludge in the top 5 cm of soil at the rate of 40 mt/ha. Incorporating the same amount of sludge in a column with an infiltration rate of 60 cm/day decreased the nitrogen removal for several cycles before the nitrogen removal stabilized at 34% which was about double the initial rate. The column with the 30 cm/day flow rate allowed sufficient detention time and mixing for denitrification of most of the nitrate whereas much of it moved through the 60 cm/day column. Infiltration rates were not affected by incorporation of sludge. Incorporation of sludge at the rate of 200 mt/ha into the top 10 cm of column 5 that was flooded with sewage water at the rate of 75 cm/day resulted in about 50% increase in the output of nitrogen from the column. This persisted for 8 cycles or until the end of the year. The combination of high sludge application rates probably caused the increased nitrogen output from the column. Therefore these columns demonstrated again that denitrification is governed by a combination of factors including infiltration rate, C:N ratio, and detention time. Sludge decomposition rates would differ in the field but the columns indicate that sludge addition would increase N removal by denitrification.

SUMMARY AND CONCLUSIONS

Thus a series of experiments on factors controlling denitrification during groundwater recharge showed that the amount of nitrogen removed was determined primarily by the carbon to nitrate – N ration in the water moving through the soil. This ratio depended upon the organic carbon content of the applied sewage water and the soil infiltration rate. Appling effluents with substantial carbon concentrations like primary sewage effluent provided more denitrification than application of low carbon content effluents like secondary sewage effluent. Nitrogen removal of any effluent could be increased by reducing the infiltration rate to promote mixing of the nitrate leached through the soil with the incoming sewage water.Denitrification was increased by mixing dry sludge with the soil to provide additional organic carbon through sludge decomposition.

Thus, this serves of experiments showed that groundwater recharge systems can be managed to minimize groundwater contamination by nitrate and an array of management techniques are available to be used where different soils, wastewaters and water quality standards are found.

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MICROBIAL ECOLOGY OF A HAZARDOUS WASTE DISPOSAL SITE: ENHANCEMENT OF BIODEGRADATION

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ABSTRACT

Pollution of ground water by organic compounds is a serious threat to the nation's water supply. Biodegradation of organic contaminants by the indigenous microbial population is one of the most effective methods for removing these contaminants. However, microbial activity in aquifers may be limited by the levels of dissolved oxygen, nutrients, or the numbers of microorganisms capable of degrading the contaminants. The effects of nutrient and oxygen addition on biodegradation were tested on ground water collected aspectically from a well at an abandoned wood-creosoting operation in Conroe, Texas. The ground water from this well is contaminated with 10-500 μg/l levels of several polynuclear aromatic compounds including naphthalene, dibenzofuran, fluorene, 2-methyl naphthalene, and phenanthrene. To one sample, nutrients (nitrogen, phosphorus, potassium, carbonate, magnesium, calcium, manganese, sulfate, and iron) and dissolved oxygen were added. To another sample, dissolved oxygen alone was added to distinguish the effects of nutrient addition. One sample was incubated under nitrogen to simulate the oxygen limited conditions found in the aquifer. A sterile control was prepared by filter sterilization and the addition of 1% sodium azide. Results from the experiment indicate that the compounds were degraded most rapidly in the sample with nutrients and dissolved oxygen, but that the overall removal was as high in the sample supplied with dissolved oxygen. There was little or no removal in the control and no microbial growth. Microbial numbers increased most rapidly in the sample with added nutrients with a concurrent drop in the concentration of the contaminants.

INTRODUCTION

Hazardous waste disposal sites are often the source of organic contamination of ground water. One of the most important mechanisms for the removal of these contaminants is microbial degradation. The presence of a microbial population containing 10^6 cells/g dry soil or greater in the unsaturated zone and shallow water tables of several aquifers has been demonstrated (Wilson *et al.*, 1983). It seems likely that a significant population will exist elsewhere. This microbial population is capable of degrading many organic compounds, but may be limited by the levels of dissolved oxygen and nutrients (Raymond *et al.*, 1976).

An abandoned wood-creosoting facility in Conroe, Texas, provided an opportunity to investigate the factors which limited the biodegradation of several polynuclear aromatic contaminants including naphthalene, dibenzofuran, fluorene, 2-methyl naphthalene, and phenanthrene. The ability of the indigenous microbial population to degrade these compounds has been demonstrated (Lee *et al.*, in press, and Wilson *et al.*, submitted). Once adaptation to the contaminants has occurred, the supply of oxygen is thought to control the biodegradation. There has been no evidence for degradation of polynuclear aromatic hydrocarbons found in wood-creosoting operations under anaerobic conditions (Ehrlich *et al.*, 1982, and Ehrlich *et al.*, 1983). This experiment was designed to show the effects of increased oxygen tension and addition of possible limiting nutrients on the degradation of the polynuclear aromatic contaminants.

MATERIALS AND METHODS

Ground water collection

Five well volumes of ground water from well #2 at the Conroe site were withdrawn and discarded to clear the wells. Well #2 shows a moderate amount of contamination and is considered to be within the plume (Wilson *et al.*, submitted). Sterile tubing was then inserted into the wells and ground water pumped directly into 12.5 l reservoirs (Figure 1).

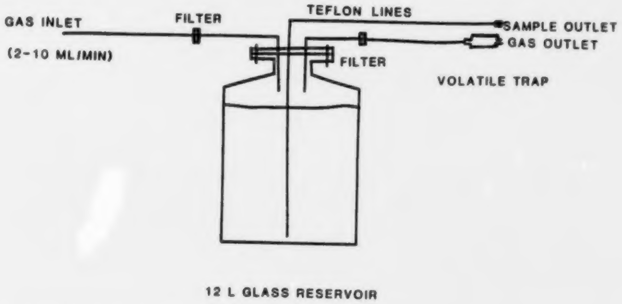

FIGURE 1. INCUBATION VESSEL

Treatment

The following treatments were used for the ground water samples:

A. Nutrients and Dissolved Oxygen Addition. The following nutrients were added: 100 mg/l $(NH_4)_2SO_4$, 40 mg/l Na_2HPO_4, 100 mg/l KH_2PO_4, 20 mg/l $MgSO_4 \cdot 2H_2O$, 2 mg/l $MnSO_4 \cdot 7H_2O$, and 0.5 mg/l $FeSO_4 \cdot 7H_2O$. Nutrient additions were based on that used by Raymond *et al.* (1978) to stimulate ground water microbes to biodegrade spilled gasoline. A compressed air atmosphere at a flow rate of 2 to 10 ml/min was maintained over the sample. The dissolved oxygen level ranged from 5.4 to 7.4 mg/l (measured with a YSI dissolved oxygen meter).

B. Dissolved Oxygen Addition. A compressed air atmosphere flowing at a rate of 2 to 10 ml/min blanketed this sample and maintained a DO of 6.4-7.4 mg/l.

C. Oxygen Limited. A nitrogen atmosphere flowing at a rate of 2 to 10 ml/min was maintained over this sample beginning about 10 hours after collection. Some dissolved oxygen was introduced during the interval before incubation began. The DO ranged from 0.7 to 1.7 mg/l.

D. Sterile Control. The sample was filtered through a series of 3.0, 0.45 and 0.2 μM filters (Gelman) to remove the bacterial population. In addition, 1% sodium azide was added. This sample was incubated under compressed air at a flow rate of 2 to 10 ml/min and the dissolved oxygen ranged from 6.4 to 7.8 ml/l.

All samples were incubated at 24°C, which is approximately the temperature of the ground water at the Conroe site.

Volatile traps

Volatile traps were made of XAD-4 resin, which has been shown to quantitatively trap organic compounds (Hutchins *et al.*, 1983).

Extraction and quantification

Sep-Pak C-18 cartridges (Waters Associates, Milford, MA) were used to concentrate the organic compounds from duplicate 25 to 150 ml samples. Methylene chloride was used to elute the organics. This procedure has been shown to be a rapid, reproducible technique for the extraction of low levels of organic compounds from ground water (personal communication, M. B. Tomson, results to be published elsewhere). Analysis was with a Varian 2600 gas chromatography instrument using an FID detector, temperature program of 50 to 250 at 10°C/min with a 4 min initial hold, injector temperature 275°C, detector 300°C, and helium carrier gas flow rate of 1 ml/min. A Hewlett-Packard ultra-performance silica capillary column with crosslinked 5%phenyl methyl silicone packing was employed. An SP-1400 integrator was used to record chromatographs.

Microbial counts

Viable counts were made on ground water medium prepared by adjusting the pH of the ground water from well #2 to 5.0, adding 1% agar and autoclaving. Following autoclaving, the concentrations of the contaminants ranged from 26-40% of their initial levels.

RESULTS AND DISCUSSION

In the sample with nutrients and dissolved oxygen additions, removal of the compounds was rapid; it was essentially complete with 12 days (Figure 2 and Table 1). The number of microbes/ml increased greatly from day 2 to day 5 in conjunction with a rapid decrease in the concentrations of the contaminants. The number of cells/ml was greater in this sample due to the utilization of additional nutrients. Raymond *et al.* (1976 and 1978) noted similar increases when gasoline contaminated ground water was supplied with nutrients. Within the 21 days that the experiment ran, 98 per cent removal or greater of the compounds was noted. It is likely that the relatively low levels of the compounds shown in Figure 2 for day 0 reflect an inaccurate measurement.

For the sample with dissolved oxygen addition alone, biodegradation rates were as rapid for naphthalene and 2-methyl naphthalene, but slower for the other compounds (Figure 3 and Table 1). However, for the entire incubation period, total removal approached that found in the sample with nutrient addition. The biodegradation rates determined in this experiment were analogous to those found previously by Lee *et al.* (in press) for ground water samples collected from other wells at the Conroe site having an adapted microbial population and incubated aerobically. Aerobic biodegradation rates for subsurface soil collected aseptically from a site near well #2 were greater than that found for the ground water alone, which may indicate the importance of the microbial population attached to sediment surfaces in removal of the compounds (Wilson *et al.*, submitted). The number of cells/ml increased to about 10^4 within 5 days. Ogawa *et al.* (1981) found a similar increase in the microbial population from an aquifer near an abandoned coal tar pit.

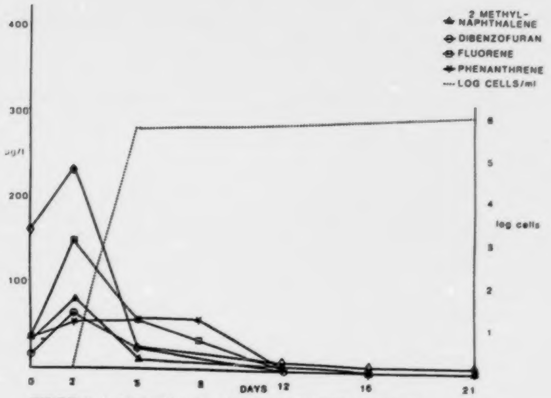

FIGURE 2. A. NUTRIENT AND DISSOLVED OXYGEN ADDITIONS

Table 1. Biodegradation Rates and Removal Efficiencies for Polynuclear Aromatics Under Various Treatments

Treatment	Naphthalene	2-Methyl Naphthalene	Dibenzofuran	Fluorene	Phenanth
		BIODEGRADATION RATES (%/week)			
A	54	52	57	54	57
B	58	56	37	33	29
C	23	16	11	0	17
D	0	0	0	0	*
		PER CENT REMOVAL			
A	98	99	100	100	100
B	99	99	94	89	81
C	69	57	12	0	27
D	0	0	0	0	*

* none detected - probably sorbed onto filter

detection limit = 1 µg/l

Treatment

A. Nutrient and Dissolved Oxygen Addition

B. Dissolved Oxygen Addition

C. Oxygen Limited

D. Sterile Control

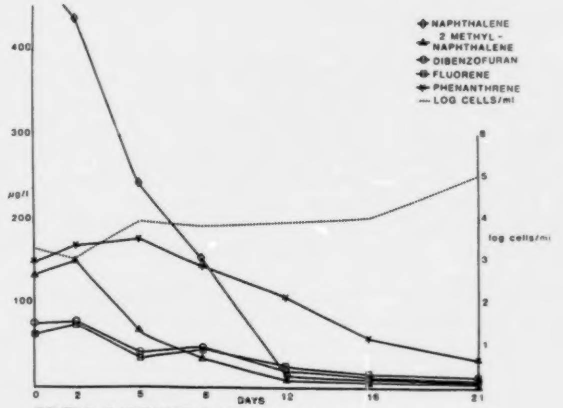

FIGURE 3. B. DISSOLVED OXYGEN ADDITION

In the oxygen limited sample, removal rates were much slower (Figure 4 and Table 1). Levels of naphthalene and 2-methyl naphthalene were reduced by about two thirds, which was probably due to the presence of dissolved oxygen introduced during the set-up of the experiment since removal slowed at the end of the incubation period as the dissolved oxygen was depleted. For complete mineralization of these contaminants, an estimated 11.3 mg/l of dissolved oxygen would be required. The minimum quantity of dissolved oxygen necessary for significant microbial action on these compounds is unknown. Dissolved oxygen tensions of 0.3 mg/l or less are found in the contaminated wells at Conroe and may support microbial activity

(Wilson *et al.*, submitted). The microbial population increased to 10^4 cells/ml, which was the same as in the sample with only dissolved oxygen, but the activity of the organisms was restricted in the oxygen limited environment.

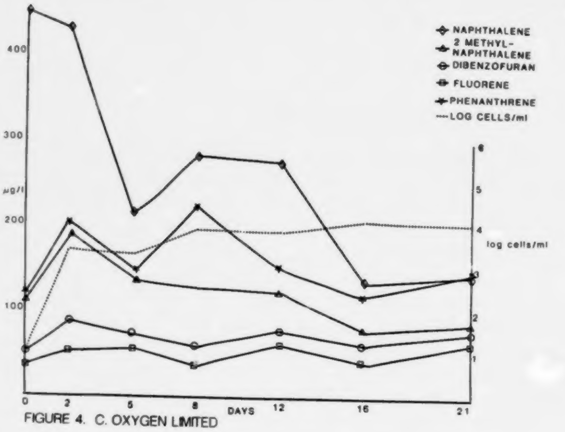

FIGURE 4. C. OXYGEN LIMITED

For the control, there was no microbial growth and no activity against the contaminants (Figure 5 and Table 1). The concentration of naphthalene showed an increase from the initial sampling period to day 8, which was probably due to analytical error. However, the concentration of the remaining contaminants remained constant during the experiment. Initial levels of the compounds were reduced by sorption onto the filter, and no phenanthrene was detected.

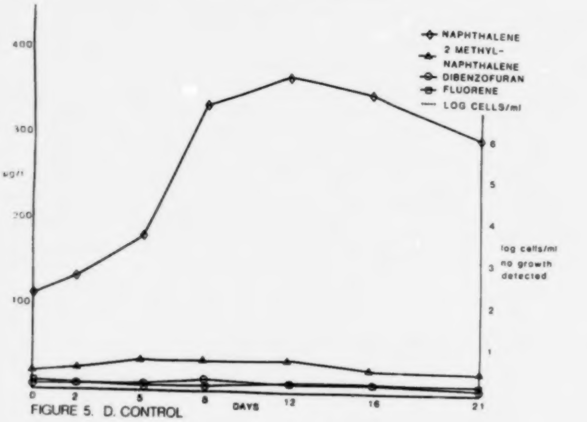

FIGURE 5. D. CONTROL

At most, 2.5% of the polynuclear aromatics were retained in the volatile traps, which shows that biodegradation was responsible for most of the reduction in their observed concentrations.

CONCLUSIONS

1. Addition of dissolved oxygen increased biodegradation.
2. Addition of possible limiting nutrients increased microbial growth and the rates of biodegradation but did not result in significantly greater removal.
3. The level of dissolved oxygen is probably the factor which limits biodegradation at the Conroe hazardous waste disposal site. The quantity of oxygen necessary for significant biodegradation of the compounds should be determined.

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ISOLATION AND GROWTH OF "NATURALLY OCCURRING" BACTERIA FROM GROUND WATER

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ABSTRACT

Ground water is an increasingly significant source of potable water and is one of the least studied ecosystems. Assessment of man's impact on this resource requires knowledge of the "naturally occurring" microbial populations. Since ground water from deep protected aquifers is generally assumed to be oligotrophic, a low nutrient medium (R2A) was selected for the primary isolation and enumeration of bacteria from well water. Of the 500 isolates recovered, >80% were Gram-negative, non-motile, rod shaped bacteria. These organisms were identified according to the three tube method of Lassen. *Acinetobacter* spp. predominated and comprised 59% of the total isolates. *Moraxella* spp., *Flavobacterium* supp., and an unidentified, oxidase negative, pigmented bacterium (PO) were also present. Direct counts using epifluorescent microscopy revealed that representative isolates grew significantly (4 orders of magnitude) in filtered well water. Enrichment of well water with low concentrations (100 ug carbon/liter or 1000 ug carbon/liter) of glucose, acetate, succinate or pyruvate enhanced the growth of the PO and *Acinetobacter* isolates.

INTRODUCTION

Ground water accounts for over 90% of the world's fresh water resources (Scalf et al, 1981) and is recognized as an important worldwide source of water for irrigation, industry, and human consumption (Todd, 1980). Although approximately 1/2 of the population of the United States relies on ground water as sole source of potable water (Zaparozec, 1979), it is one of the least studied ecosystems.

While assessment of ground water quality traditionally has focused on the detection of coliform bacteria, information concerning the non-coliform bacteria present in well water is limited. Current standard methods for the enumeration of bacteria in water rely on artificial media rich in organic compounds. The chemical characterization of ground water however indicates that nutrients available to microorganisms are present only in very low concentrations (Matthess, 1982). Organisms that inhabit ground water then must be capable of metabolism at limiting nutrient concentrations. Organisms living at organic concentrations ≤ 15 mg carbon/liter are termed oligotrophs (Kuznetsov et al., 1979).

Potentially pathogenic non-coliform microorganisms capable of oligotrophic life may be introduced to the subsurface during well drilling (McNabb, 1975) and establish resident populations which would go undetected with the standard methods of bacterial analysis of water. Investigators have detected *Pseudomonas* spp., *Flavobacterium* spp., *Acinetobacter* spp., *Aeromonas* spp., *Moraxella* spp., *Alcaligenes* spp., and *Actinomyces* spp. in water samples with isolates surviving extended periods in low nutrient concentrations (Carson et al, 1973; Henriksen, 1973; Lamka et al, 1980; van der Kooij, 1980, 1981). Their presence in the subsurface could lead to the establishment of populations capable of rapid and significant impact. Therefore, the identification and characterization of either autochthonous or transient non-coliform bacteria in well water is essential in understanding the overall quality of the water.

The purpose of this study was to enumerate, isolate, and identify the heterotrophic bacteria present in well water and to monitor selected isolates for growth in filtered and carbon enriched well water.

MATERIALS AND METHODS

Well water samples were collected for culture from two wells located on the campus of the University of Arizona, Tucson, Az. Triplicate spread plates of R2A medium were inoculated with 0.1 ml of asceptically collected well water. Cultures were incubated aerobically at 26 C. After 7 days incubation, counts were made with the aid of a stereoscope (35x) and colonies from a plate most representative of the average colony count were measured and subcultured to R2A for an additional 5 day incubation at 26 C. Surviving subculture isolates were classified according to gram reaction and oxidase tests. Gram-negative rod shaped bacteria were further identified using the Lassen three tube method (Lassen, 1975).

Selected isolates were serially transferred in filtered (0.2um) well water (FW) for a minimum of 30 days prior to inoculation into FW and FW enriched with low concentrations (100 ug C/L or 1000 ug C/L) of glucose, acetate, succinate or pyruvate. Growth was monitored by the Acridine Orange Direct County (AODC) method of Hobbie et al. (1977).

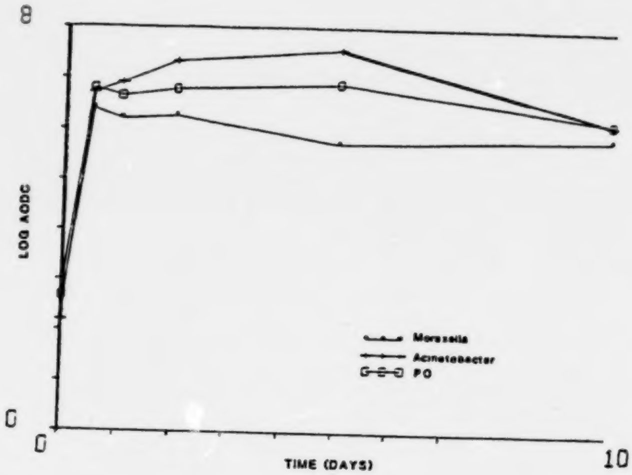
RESULTS AND DISCUSSION

Well #1 averaged 234 colony-forming units (cfu)/ml well water and Well #2 averaged 508 cfu/ml. Gram-negative rod shaped bacteria within a limited number of genera predominated. A total of 511 isolates from the two test wells were identified (Table 1). *Acinetobacter* spp. and a yellow to yellow-orange pigmented, non-motile, oxidase negative gram-negative rod (PO) were consistently isolated. Isolates identified as belonging to *Moraxella* sp. and *Flavobacterium* sp. were sporatically isolated from the two wells. Gram positive organisms occurred in low numbers and did not exceed 10% of the total number of bacteria isolated. Approximately 9% of primary isolates did not grow on subculture to R2A. Growth of the selected isolates in FW revealed rapid, significant increases in bacterial numbers within 12 hours (Figure 1).

TABLE 1. IDENTIFICATION OF WELL WATER ISOLATES

	Well 1		Well 2	
Organism Isolated	No.	%	No.	%
Acinetobacter sp.	183	71.21	95	37.40
PO	29	11.28	36	14.17
Moraxella sp.	7	2.92	38	14.96
Flavobacterium sp.	9	3.50	29	11.42
Psuedomonas/*Alcaligenes*	1	0.39	3	1.18
Gram-Positive Rods	7	2.72	17	6.70
Gram-Positive Cocci	3	1.17	4	1.57
No Growth on Subculture	18	7.00	32	12.60
Total Number of Isolates	257		254	
Average Number of Bacteria Isolated/ml	234		568	
% Gram-Negative Rods	89.10		79.13	

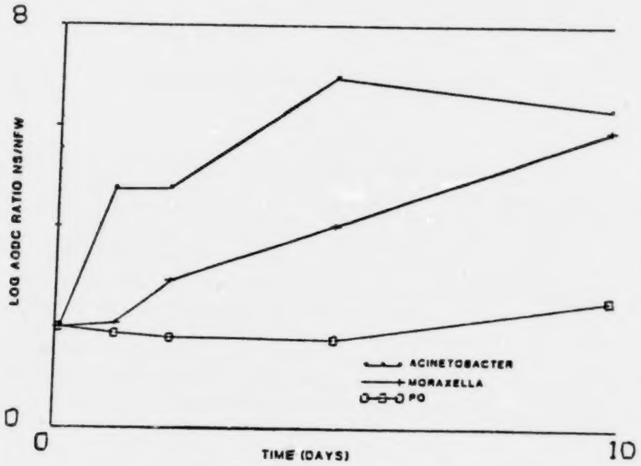
FIGURE 1



GROWTH OF ISOLATES IN FILTERED WELL WATER

Carbon enriched FW further stimulated the growth of the *Acinetobacter* sp. and PO isolates, but failed to enhance the growth of *Moraxella* sp. (Figure 2).

FIGURE 2



GROWTH OF ISOLATES IN ORGANIC-C ENRICHMENT

The presence of a significant number of non-coliform opportunistic pathogenic organisms in well water and the ability of *Acinetobacter* sp. to utilize carbon compounds in low concentrations poses a potential health hazard. This rapid and sustained growth within a 24 hour period reflects the ability of these bacteria to not only survive as transitory organisms but to establish resident populations in dilute environments. The impact these microorganisms may have on subsurface environments and their potential public health threat require further study.

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BIODEGRADATION OF HALOAROMATIC SUBSTRATES IN A SHALLOW ANOXIC GROUND WATER AQUIFER

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ABSTRACT

Anaerobic ground water aquifers receive a variety of xenobiotic contaminants, but the eventual fate of these chemicals is uncertain. We investigated whether several halogenated benzoates, phenols and phenoxy-acetic acid herbicides could be degraded in microcosms inoculated with anoxic aquifer material sampled from two sites near the municipal landfill in Norman, Oklahoma. One site was actively methanogenic, whereas carbon flow in the other site was apparently dominated by sulfate-reducing processes. After two months, benzoate and phenol were completely metabolized in samples from both sites, but phenoxyacetate persisted in sulfate-reducing microcosms. The methanogenic aquifer samples showed more than 80% conversion of 9 of 10 halobenzoates, 5 of 7 chlorophenols, and 2 of 2 phenoxyacetic acid herbicides. The sulfate-reducing aquifer samples showed no ability to transform the halogenated substrates during the initial period. High pressure liquid chromatography and mass spectral evidence indicated that the primary degradation pathway for these chemicals involved the loss of an aryl halide and its substitution by a hydrogen atom. Complete dehalogenation was required before the substrates could be completely mineralized. These results indicate that the microflora of anozic aquifers have the potential to reductively metabolize xenobiotic chemicals under the proper environmental conditions.

INTRODUCTION

The past 40 years of research have taught us much about the ability of microorganisms to transform xenobiotic contaminants in nature. To oversimplify, it can be stated that the metabolic fate of such chemicals is influenced by (a) the structure of the particular pollutant, (b) the biochemical versatility of the indigenous microflora, and (c) the existing environmental conditions. Each of these factors can alone or in combination help to retard or stimulate biodegradation activity. However, the effect of these factors on pollutant biodegradation in the subsurface is not well studied despite increased incidents of ground water contamination throughout the world. Thus, the feasibility of extrapolating biodegradation information obtained from other environments to the subsurface is often questioned.

Of particular concern is the widespread use and release of halogenated aromatic chemicals. These compounds are often toxic, tend to resist conventional treatment processes, can bioaccumulate and alter the normal cycling of carbon in some ecosystems. Research has shown that many haloaromatic substrates can be biologically transformed in a variety of habitats (Alexander, 1981; Kobayashi, and Rittmann, 1982), but initial bioconversions often result in intermediates which remain environmental problems til the aryl halides are released in inorganic form. However, little is known about the ability of ground water microorganisms to catalyze such transformations.

Therefore, we investigated the fate of a variety of halobenzoates, chlorophenols and chlorophenoxyacetic acids in samples taken from a shallow aquifer bordering a municipal landfill. High pressure liquid chromatography (HPLC), gas chromatography (GC) and mass spectral evidence indicated that chemicals from each of the tested classes could be dehalogenated and subsequently mineralized. However, this process only occurred rapidly in aquifer samples which were actively methanogenic.

MATERIALS AND METHODS

Samples were taken from two sites within the shallow anoxic aquifer bordering the South Canadian River in Norman, Oklahoma (Figure 1). The two sampling sites, designated sulfate-reducing (S) and methanogenic (M), were contaminated with leachate from the local municipal landfill. Aquifer solids from both sites were obtained and anaerobic serum bottle microcosms constructed as previously described (Suflita and Miller, 1984).

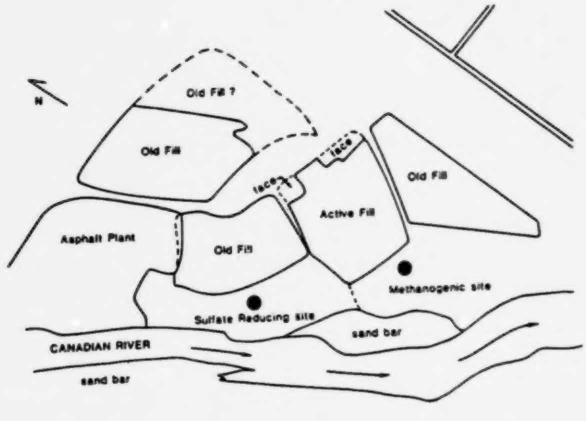

Figure 1. A map of the Norman municipal landfill showing the two sites sampled for this study.

The liquid phase of the microcosms was monitored by reverse phase HPLC for the removal of substrates and the appearance of metabolites as previously described (Suflita and Miller, 1984). Methane formation above unamended controls was monitored by gas chromatography (Suflita and Miller, 1984). Metabolite identification was made by HPLC cochromatography or by mass spectral comparison of the isolated metabolite with authentic chemicals. Sulfate was analyzed on the aqueous phase of the microcosms by ion-exchange HPLC and detected with a Wescan Model 213 conductivity detector. Autoclaved microcosms served as sterile controls and were uniformly unable to transform any of the tested substrates.

RESULTS AND DISCUSSION

Field Observations

Inoculum for anaerobic microcosms was obtained from two sites bordering the municipal landfill in Norman, Oklahoma (Figure 1). The two sites (S and M) were spatially separated by about 150 yards and differed in their chemical and physical characteristics (Table 1).

Aquifer solids at the M site were typical of an alluvial sand whereas the solids at the S site were colored grey to black (Table 1). Since the S site also had a slight sulfide odor, we speculated that the dark coloration was possibly due to iron-sulfide precipitates.

In contrast, the M site exhibited an obvious volatile fatty acid odor, and dissolved oxygen could not be detected. Bore holes actively evolved a gas which was later identified as CH_4. However, no significant CH_4 evolution could be detected from similar bore holes at the S site. These observations suggested that the terminal metabolic process at the S site was primarily sulfate reduction while methanogenesis predominated at the M site.

The Effect of Sulfate on Methanogenesis in Microcosms

In earlier studies, we found that microcosms using M aquifer solids as inoculum were actively methanogenic. However, similar microcosms using S solids produced methane at a rate approximately three orders of magnitude slower (Sulflita and Miller, 1984). This observation, in conjunction with the field observations, suggested that sulfate concentrations at the two sites may be an important factor influencing the flow of carbon in the aquifer.

Observation	Sulfate-Reducing Site	Methanogenic Site
pH	7.2-8.3	6.9-7.5
Temperature	4-20°C	8-20°C
Aquifer Solids	Dark Grey to Black Color	Sandy Color
Odor	Petroleum/Sulfide	Volatile Fatty Acids
Dissolved Oxygen	2 ppm	Undetectable
Gas Evolution	No	Yes

Table 1. A comparison of the field observations made at the two sites sampled for this study.

When ground water from both sites was assayed for inorganic anions, no nitrate or nitrite was detected at either site. However, sulfate levels ranged from 200-350 ppm at the S site while only 30-40 ppm was found at the M site.

When 200 ppm inorganic sulfate was added to the actively methanogenic M microcosms, endogenous CH_4 rates were significantly inhibited (Figure 2B). However, the same levels of sulfate had no effect on the already low rates of methanogenesis in S microcosms (Figure 2A).

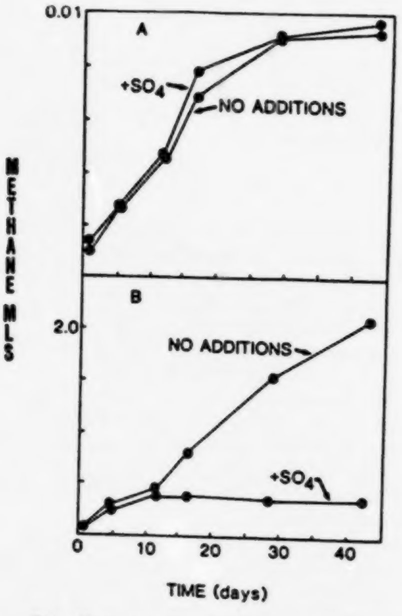

Figure 2. The effect of sulfate on the endogenous rates of methanogenesis occuring in microcosms made from (a) sulfate-reducing or (b) methanogenic aquifer material.

These results support findings from other studies which conclude that high levels of sulfate can inhibit methanogenesis (Abram and Nedwell, 1978a, b; Smith and Klug, 1981; Lovely, et al., 1982; Oremland and Polcin, 1982). The most plausible explanation for these observations is that sulfate-reducing organisms outcompete methanogens for available electron donors in sulfate rich habitats. A variety of recent studies have shown that sulfate-reducers have a lower Michaelis half-saturation constant (K_m) and thus higher affinities for electron donors such as acetate and H_2 (Abram and Nedwell, 1978a, b; Lovely, et al., 1982; Kristjansson, et al., 1982; Schonheit, et al., 1982; Robinson and Tiedje, 1984). In high sulfate environments, the pool sizes of electron donors are presumably too low to permit methanogens to compete effectively.

Biodegradation of Haloaromatic Substrates

The differences in physiochemical characteristics of the two aquifer sites provided the opportunity to investigate the biodegradation of selected substrates under both sulfate-reducing and methanogenic conditions. We therefore incubated a variety of halogenated benzoates, phenols or phenoxyacetates in either S or M microcosms. A summary of these incubations is seen in Table 2.

Table 2. Substrates tested for anaerobic biodegradation potential in a landfill leachate contaminated aquifer

Substrate	% Substrate Remaining in Microcosms Sulfate-Reducing Site Incubation time (weeks) 0	4	8	Downgradient Site 0	4	8	12
Benzoate	100	5	0	100	2.5	0	—
3-chlorobenzoate	100	—	95	100	98	2.1	3
4-chlorobenzoate	100	—	100	100	—	97	—
2-bromobenzoate	100	—	100	100	—	0	—
3-bromobenzoate	100	—	100	100	—	0	—
4-bromobenzoate	100	—	100	100	—	0	—
2-iodobenzoate	100	—	73	100	—	0	—
3-iodobenzoate	100	—	98	100	—	0	—
4-iodobenzoate	100	—	69	100	—	0	—
3,4-dichlorobenzoate	100	—	102	100	—	94*	—
3,5-dichlorobenzoate	100	—	101	100	76	0	0
Phenol	100	48	15.6	100	6	0	0
2-chlorophenol	100	—	88	100	12	3	9
3-chlorophenol	100	—	100	100	111	10	0
4-chlorophenol	100	—	100	100	112	36	4
2,4-dichlorophenol	100	—	59	100	16	0	0
2,5-dichlorophenol	100	—	57	100	63	7	3
3,4-dichlorophenol	100	—	119	100	102	96	95
2,4,5-trichlorophenol	100	—	75	100	—	73	—
Phenoxyacetate	100	—	98	100	—	0	—
2,4-dichlorophenoxyacetate	100	—	107	100	52	4	0
2,4,5-trichlorophenoxyacetate	100	—	106	100	7	2	2

*No substrate detectable after 20 weeks of incubation.

The benzoate moiety easily disappeared in microcosms from either site but methane levels above unamended controls were detected only from M microcosms. Benzoate is well known to completely degrade in a variety of anaerobic habitats by methanogenic consortia (Tarvin and Buswell, 1934; Ferry and Wolfe, 1976; Healy and Young, 1979). More recently, benzoate as well as other aromatic acids have been found as suitable electron donors for sulfate-reducing bacteria (Pfenning and Widdel, 1981). It is therefore not surprising that benzoate was rapidly removed from both types of aquifer microcosms.

Large differences were observed in the ability of the aquifer microflora to transform halogenated benzoates. For instance, a variety of chloro- bromo- and iodobenzoates completely disappeared in M microcosms while the same substrates tended to persist in S microcosms (Table 2). Only 4-chlorobenzoate and 3,4-dichlorobenzoate persisted in M microcosms after 3 months incubation. However, 3,4-dichlorobenzoate did disappear with increased incubation (between 3 and 5 months).

In addition to substrate removal, we also observed the appearance of metabolites in the M microcosms. The metabolites cochromatographed with authenic chemicals that were at least one halogen less than the parent substrates. For instance, 3-chlorobenzoate was observed as a metabolite when 3,5-dichlorobenzoate served as the starting substrate and benzoate was found as an intermediate in the metabolism of 3-chlorobenzoate. No intermediates were observed in S microcosms.

Phenolic compounds exhibited degradation patterns similar to the benzoates. Phenol disappeared rapidly from both types of microcosms. However, only M microcosms showed the removal of a variety of mono- and dichlorophenols. Similarly, dehalogenated intermediates were detected in these incubations and identified by HPLC co-chromatography and mass spectrometry (Suflita and Miller, 1984). The small amount of chlorophenol removal in S microcosms and 2,4,5-trichlorophenol and 3,4-dichlorophenol loss from M microcosms cannot be correlated with significant intermediate formation. These compounds may possibly be degrading by an alternate pathway in S microcosms or removed through an unknown physiochemical process.

Unlike benzoate and phenol, phenoxyacetate could not be removed in S microcosms while M microcosms rapidly mineralized this substrate to CH_4 and CO_2. In addition only M microcosms were only to dehalogenate and mineralize the herbicides 2,4-dichlorophenoxyacetate (2,3-D) and 2,4,5-trichlorophenoxyacetate (2,4,5-T) (Table 2). Partially dehalogenated phenoxyacetates and halogenated phenols were detected as intermediates with these substrates.

SUMMARY

Results from this study demonstrate that a variety of mono-, di- and trihalogenated aromatic substrates can be transformed by the microflora indigenous to a shallow anoxic aquifer. The proposed biodegradation pathway associated with this metabolism is shown in Figure 3. Under methanogenic conditions, benzoates, phenols and phenoxyacetate substrates can be dehalogenated to form intermediates that are at least one halogen less than the parent chemical. Complete removal of the aryl halides is required before the aromatic ring can be mineralized to CH_4 and CO_2. With herbicides like 2,4,5-T, dehalogenation appears to be the primary metabolic event and results in a dichloro- or monochloro-intermediate. However, subsequent reactions involve the hydrolytic conversion of the intermediate to the corresponding chlorophenol and eventually to phenol which can then be mineralized.

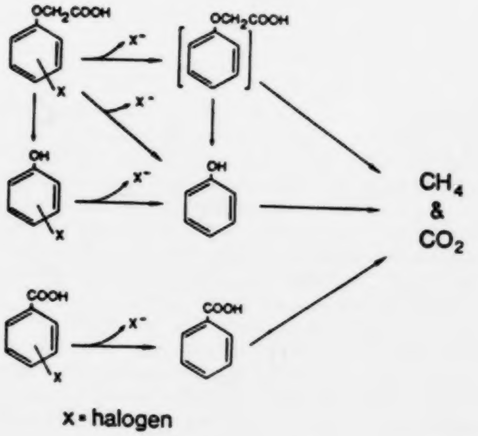

Figure 3. Proposed degradation pathway for the anaerobic metabolism of halogenated aromatic substrates in methanogenic aquifers.

The metabolic fate of these substrates in sulfate-reducing aquifers is unclear. However, similar dehalogenation reactions seem to be drastically inhibited or prevented entirely.

These reactions are identical to earlier studies on the anaerobic dehalogenation of halobenzoates (Suflita, et al., 1982) and halophenols (Boyd and Shelton, 1984). Thus, this study suggests that biodegradation information generated in other habitats can be selectively extrapolated to anoxic subsurface environments.

ACKNOWLEDGMENTS

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SORPTION PROCESSES

SORPTION OF ORGANIC SOLUTES: COMPARISON BETWEEN LABORATORY-ESTIMATED RETARDATION FACTORS AND FIELD OBSERVATIONS

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ABSTRACT

This work presents the results of laboratory experiments developed to measure sorption distribution coefficients for five organic solutes and aquifer materials. The aquifer material was excavated from the site of a field experiment, where the transport of halogenated organic solutes under natural conditions is being studied. The solutes used in the field study, carbon tetrachloride, bromoform, tetrachloroethylene, 1,2 dichlorobenzene and hexachloroethane, were also used in the laboratory experiments. Isotherms measured for these solutes in the concentration up to 0.08 $g \cdot m^{-3}$ were linear and had near zero intercepts. Retardation factors inferred from the isotherms for carbon tetrachloride, bromoform and tetrachloroethylene were within the range of retardation factors observed in the field. The rank order of the distribution coefficients was in agreement with the solutes' octanol water partition coefficients.

INTRODUCTION

Contamination of ground water by persistent trace organic solutes has recently become a problem of widespread concern. To address this problem, a group of investigators from Stanford University and the University of Waterloo are conducting a large scale natural gradient field experiment. In August 1982, a suite of five organic solutes and two inorganic tracers were injected into an uncontaminated portion of an unconfined, glaciofluvial sand aquifer at Canadian Forces Base Borden in Ontario, Canada. Transport of the solute plume was monitored with a three dimensional array of sampling wells. Furthermore, three wells were frequently monitored to provide breakthrough curves for the tracers and organic solutes. Details of the experimental field site have been presented elsewhere (Mackay et al, 1983a), as have preliminary interpretations of the field results (Mackay et al, 1983b, Freyberg et al, 1983).

In conjunction with the field experiment, numerous laboratory studies have been undertaken to assist in interpreting the field results. The objective of this work was to conduct batch sorption isotherm studies to determine the extent to which sorption of the trace organic solutes explains the observed retardation in the field.

BACKGROUND

Transport of a sorbing solute in an aquifer is retarded relative to the movement of the ground water by a factor known as the retardation factor, R (Freeze and Cherry, 1979). R, is the velocity of a sorbing solute relative to the velocity of the ground water. Bear (1979) shows that a linearly sorbing but non-reacting solute at local equilibrium (i.e., no mass transfer limitations) has a retardation factor given by

$$R = 1 + \frac{\rho K_d}{n} \qquad (1)$$

where ρ = bulk density of the aquifer ($g \cdot m^{-3}$)
n = void fraction
K_d = distribution coefficient ($m^3 \cdot g^{-1}$)

ρ and n are aquifer properties which do not vary to the extent that K_d does; therefore R depends strongly on K_d. Under the assumption of linear sorption equilibrium, K_d is the slope of the isotherm. Consequently, R may be estimated by measuring a batch isotherm for material from an aquifer of known ρ and n, provided the assumptions noted above are valid.

The retardation factor may also be estimated from field observations of breakthrough curves, as discussed by Roberts et al. (1980, 1981) and Mackay et al. (1983b). In this case, R is determined by taking the ratio of the travel time of the center of mass of a conservative tracer (e.g., chloride) to a sampling well to the travel time of the center of mass of the sorbing solute.

MATERIALS AND METHODS

Aquifer material for the batch isotherm studies was excavated in June 1983 from a location 11.5 m east of the experimental plume. Approximately 380 kg of aquifer material was removed from below the water table and at a depth in the range of the experimental plume. The site has distinct small-scale (1-10 cm) horizontal bedding with only weak lateral continuity. Therefore, we believe that the sample is representative of the aquifer material at the experimental site. The excavated aquifer material was transported to Stanford University where it was air-dried, completely homogenized and divided with a riffle sample splitter into 500 g subsamples for storage. The aquifer material was stored at room-temperature in the dark until used.

The aquifer material is characterized by sub-angular to well-rounded grains that are moderately well sorted. The mineralogical composition of the sand is listed in Table 1. It is important to note that the organic carbon content is below 0.1% (Table 1), a lower limit below which mineralogical surface area may become important in influencing K_d as well as governing the form of correlations developed to estimate K_d (Schwarzenbach and Westall, 1981).

Table 1. Composition of the Borden Aquifer Material

	Binocular Microscope[1]	X-Ray Diffraction[2]
Quartz	40-50 %	58%
Amphiboles	15-20%	7%
Feldspars	15-25%	19%
Carbonates	8-10%	14%
Biotite	<5%	*
Other	<5%	2% chlorite
organic carbon[3]	**	0.02%
specific surface area[4]	**	0.8 m^2/g

[1] Dance, J. T. (1980)
[2] determined by a petrological consultant except as noted
[3] persulfate digestion technique
[4] BET-Krypton analysis
* not detected
** not determined

The water used in the sorption experiments was chosen to reflect the ionic composition of the native ground water at the experimental site. Organic-free, deionized-water was supplemented with major ions and saturated with calcium carbonate at atmospheric partial pressure of CO_2. This synthetic ground water inhibited dissolution of minerals and facilitated centrifugation.

The five organic solutes used in both the field experiment and the laboratory studies include carbon tetrachloride (CTET), bromoform (BROM), tetrachloroethylene (PCE), 1,2 dichlorobenzene (DCB), and hexachloroethane (HCE). These solutes, with the exception of bromoform, were purchased as ^{14}C-radiolabelled solutes. Several methanol stock solutions of various concentrations of each of these solutes were made, and stored at 4°C until use.

The batch experiments were conducted in 40 ml glass centrifuge tubes equipped with an open-hole cap and a teflon-faced silicone septum. The centrifuge tubes were filled with approximately 45g of aquifer material and then saturated with synthetic ground water to remove all head space. Various volumes of a solute-methanol solution were injected through the septum with a micro-syringe. The volume of methanol injected was limited such that the mole fraction of methanol never exceeded 5×10^{-4}. The organic solute concentrations were in the range observed in the field. Samples were equilibrated on a rotary tumber, centrifuged at 2500 rpm for 30 minutes, after which the supernatant was removed for analysis.

In the case of the ^{14}C-labelled solutes, approximately 2.5 ml of supernatant were syringe pipetted into 10 ml of Instagel Liquid Scintillation Cocktail (Packard) and counted with a Packard Tricarb Model 4530 Scintillation Counter. Bromoform was analyzed by GC analysis of a pentane extract (Trussell et al, 1979), obtained from a 10 ml sample of supernatant. A 5 μl aliquot was injected into a Tracer Model 220 gas chromatograph, equipped with a packed column and a linearized ^{63}Ni detector.

Sorption experiments conducted by the technique outlined above depend on measuring a decrease in aqueous concentration of the organic solute to determine the amount of sorption. One of the weaknesses of this technique is that a loss of the solute from the system would be mistaken for sorption. Therefore, mass balances were performed for the radiolabelled solutes to determine the amount of solute remaining at the end of the sorption experiment. These mass balances were performed by displacing 5 mls of supernatant with 1-octanol and equilibrating the sample for one day. An aliquot of the octanol was taken for liquid scintillation counting. At the end of the experiment, the activity that could be accounted for in the displaced supernatant and the 1-octanol allowed us to calculate a mass balance.

RESULTS

To determine the time required to reach equilibrium, preliminary rate studies were undertaken with each radiolabelled solute. The results from these rate experiments are presented in Figure 1. The approach to equilibrium is relatively slow, requiring several days, which is consistent with data of Karickhoff (1981). Based on results presented in Figure 1, we chose 3 days as the equilibration time for HCE, DCB and PCE, and 2 days for CTET. Equilibrium isotherms measured for bromoform showed no significant change resulting from equilibration times of 1 and 2 days. Consequently, the time for equilibration of bromoform was selected to be two days.

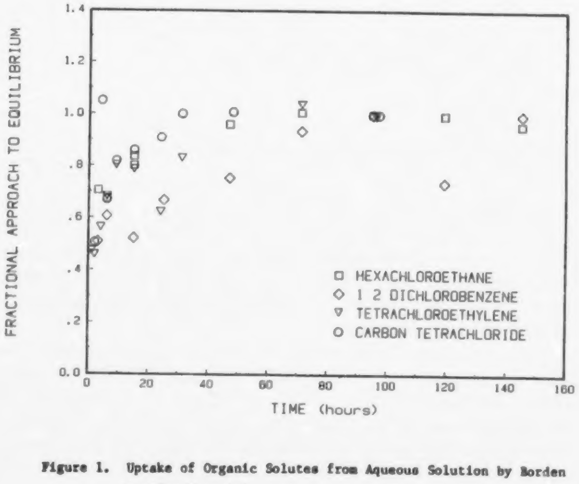

Figure 1. Uptake of Organic Solutes from Aqueous Solution by Borden Aquifer Material.

The equilibrium isotherm for carbon tetrachloride is presented in Figure 2. The close agreement between the different symbols in Figure 2, which refer to duplicate experiments, shows that the technique is reproducible. In addition, the isotherm is linear ($r^2 = 0.961$) and the intercept is not significantly different from zero at the 95% confidence level. Error bars plotted in Figure 2 are the result of random error propagation calculations; these experimental errors were approximately equal for all of the radiolabelled solute studied. Therefore, the relative error was lower for more strongly sorbed solutes than for weakly sorbed ones.

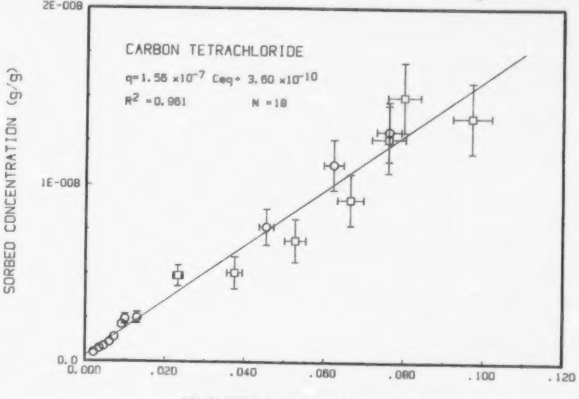

Figure 2. Equilibrium Isotherm for Carbon Tetrachloride and Borden Aquifer Material.

The relative relationships between the five isotherms are shown on Figure 3. The lines plotted result from a least squares fit of the experimental data. The slopes of these isotherms (e.g., K_d), the intercepts, and correlation coefficients are summarized in Table 2.

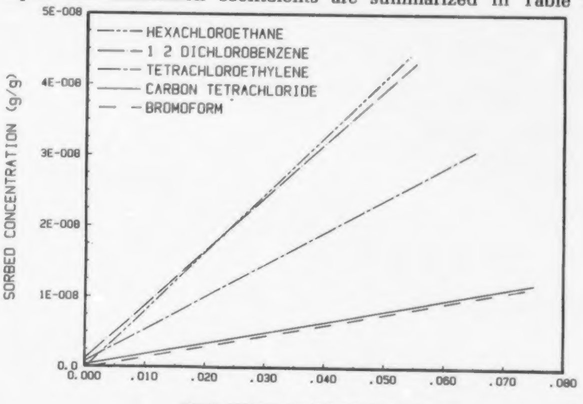

Figure 3. Equilibrium Isotherms for Five Organic Solutes and Borden Aquifer Material.

Table 2. Isotherm Results

Compound	$K_d \times 10^7$ $(m^3 \cdot g^{-1})$ ±95% Confidence Interval	Intercept (g/g) $\times 10^9$ ±95% Confidence Interval	r^2	n*
Carbon Tetrachloride	1.56±0.16	0.36±0.81	.961	18
Bromoform	1.57±0.42	-0.12±0.78	.889	12
Tetrachloroethylene	4.60±0.33	0.85±0.93	.970	24
1,2 Dichlorobenzene	7.63±0.30	1.26±0.60	.992	24
Hexachloroethane	8.22±0.35	-0.10±0.20	.982	38

* n = no of samples

Correlation coefficients for the radiolabelled solutes all exceed 0.961. Hence, the data plotted in Figure 2 represent the case of poorest linear fit for the ^{14}C solutes. Data for bromoform are more scattered due to the greater variability of the gas chromatography analysis. All intercepts are not statistically different from zero at the 95% confidence level, with exception of DCB, which is indistinguishable from zero at the 90% confidence level.

To assess the influence of methanol on the sorption of trace organic solutes, a series of three-point isotherms were measured for mole fractions of methanol ranging from 9×10^{-5} to 10^{-2}. Model calculations show that of the compounds studied in this work, HCE (the least polar solute) is most strongly influenced by methanol (Munz, 1983). Consequently, three point isotherms were measured for HCE by running triplicates for a single point on the isotherm and then assuming a zero intercept. The results, plotted on Figure 4, show that the distribution coefficient is insensitive to methanol concentrations up to mole fractions of 10^{-3}, a concentration factor of 2 greater than that achieved in the equilibrium studies.

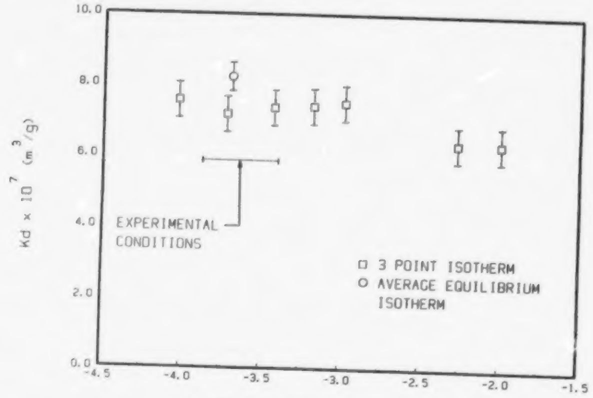

Figure 4. Dependence of the Distribution Coefficient on Methanol Concentration.

Results from the mass balance experiments performed by the 1-octanol extraction technique are presented in Table 3. In all cases, 91% or more of the solute injected could be recovered after equilibration. Although it is uncertain whether the amount of solute not recovered was lost from the system or not extracted from the sand, the results nevertheless suggest that most of the solute assumed to be sorbed was still in the system.

Table 3. Mass Balance Results

	% Recovery
Carbon Tetrachloride	92
Tetrachloroethylene	91
1,2 Dichlorobenzene	94
Hexachloroethane	95

DISCUSSION

As stated above, the major objectives of this work were to determine the extent to which sorption of organic solutes explains observed field retardation of the same solutes relative to chloride tracer. To make a comparison between field and laboratory data, we have calculated retardation factors for the five organic solutes from equation 1 and the isotherm results, presented in Table 2. These calculated retardation factors, along with those determined from the breakthrough curves, are listed in Table 4. Where comparisons are possible, namely for CTET, BROM and PCE, the agreement is remarkably close. Consequently, linear, reversible sorption does explain the behavior of these solutes at the experimental field site. In the cases of DCB and HCE, there were insufficient breakthrough data to determine retardation factors, as other processes appear to be affecting the transport of these organic solutes.

Table 4. Comparison of Retardation Factors

	Experimental*	Breakthrough Curve
Carbon Tetrachloride	1.7±0.1	1.5-1.8
Bromoform	1.7±0.2	1.5-1.8
Tetrachloroethylene	3.1±0.1	2.4-3.7
1,2 Dichlorobenzene	4.4±0.2	**
Hexachloroethane	4.7±0.2	**

* $\rho = 1.7 \times 10^6$ g·m^{-3}
n = 0.38
** insufficient breakthrough curve data

The distribution coefficients of organic solutes sorbed to aquifer materials have been successfully correlated to the 1-octanol-water partition coefficient, K_{ow} (Schwarzenbach and Westall, 1981). The distribution coefficients presented in Table 4 follow the trend predicted by these correlations; K_d increases with increasing hydrophobicity or K_{ow}. However, based on K_{ow} alone, we would expect the distribution coefficient for HCE to be at least a factor of 2 larger than that for DCB. This apparent anomaly may be related to the low organic carbon content of the aquifer material. Additional work is required to explain these observations.

It should be noted that the close agreement between the laboratory results and field observations for CTET, BROM and PCE may be an consequence of the experimental design. The field site was chosen in part because of the relative homogeneity of the aquifer material. Furthermore, a large bulk sample was obtained which would minimize the effect of the distinct small scale horizontal bedding. In systems confounded by more complicated geology, such close agreement between field and laboratory results is likely to be harder to attain.

ACKNOWLEDGMENT

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QUINOLINE PARTITIONING IN SUBSURFACE MATERIALS – ADSORPTION, DESORPTION, AND SOLUTE COMPETITION

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ABSTRACT

The adsorption/desorption behavior of quinoline, a basic N-heterocycle common to energy-derived liquid and solid waste, was evaluated at low solution concentration (0.066μg/ml-12.9 μg/ml) on nine subsoil materials. The subsoils were low in organic carbon and varied in pH, texture, and chemical properties. Adsorption was studied under nitrogen using 0.01 $\underline{M}$ $CaCl_2$ as an electrolyte. The adsorption isotherms were curvilinear and were adequately represented by the Freundlich equation. Subsoil pH was the dominant factor that influenced quinoline sorption. Adsorption was high (>95%) in acidic subsoils (pH <6) and low in basic subsoils (pH >7). Quinoline sorption did not correlate with subsoil organic carbon content, surface area, or clay content. The desorption of quinoline showed significant hysteresis in both an acidic and basic subsoil. However, hysteresis was significantly less in the basic subsoil, suggesting 4-6 greater sorption reversibility. The effect of pyridine (at 1,5, and 10 μg/ml), a single ring basic N-heterocycle, on the sorption of quinoline (0.26μg/ml-12.9 μg/ml) was examined. Quinoline sorption on a basic subsoil was uneffected by the presence of pyridine. Pyridine reduced quinoline sorption on an acidic subsoil, with the greatest effect occurring at low quinoline concentrations.

INTRODUCTION

Basic N-heterocyclic compounds are found in many energy-derived waste materials. Quinoline is a common N-heterocycle in energy wastes and is a possible liver carcinogen. The soil or subsurface adsorption of multi-ring basic N-heterocycles has not been investigated in detail. Limited research with quinoline analogs suggest the importance of organic material in adsorption (Banwart et al., 1982), while studies with quinoline and layer lattice silicates demonstrate the importance of cationic adsorption and pH in quinoline retention (Helmy et al., 1983, Doehler and Young, 1961). The objective of this research was to investigate quinoline adsorption on a variety of subsurface materials low in organic carbon to determine prominent mechanisms of retention and to evaluate the influence of important subsoil and solution phase properties. Results are presented for adsorption and desorption on subsoils of different chemical characteristics, the effects of solution composition and ionic strength, and competitive interactions with pyridine, another basic nitrogen aromatic heterocycle.

EXPERIMENTAL PROCEDURES

Methods

Sorption studies were carried out in a batch mode under N_2 atmosphere at 25°C in 25 ml Corex (Pyrex brand) high-speed centrifuge tubes using 2 g of soil and 10 ml solution. The soil was preequilibrated with .01 $\underline{M}$ $CaCl_2$ for 4 hr prior to the addition of quinoline. Varying quantities of cold quinoline standards were added to the soil solutions along with a fixed quantity of ^{14}C-quinoline (approximately 50,000 dpm). The initial concentration of quinoline ranged from 50 ppb to 13 ppm. Each concentration was run in duplicate. After the addition of the quinoline, the centrifuge tubes were agitated in an incubator/shaker for 24 hr. Kinetic studies had shown that equilibrium was attained in less than 18 hr. At the end of the incubation period, the tubes were centrifuged at 7500 x g for 15 min and the supernatant analyzed for radioactivity by liquid scintillation counting. The quantity of quinoline sorbed was determined by the difference in initial and final solution radioactivity measurements.

Desorption measurements were made by conducting the sorption experiments as described above. After the 24 hr incubation period under N_2 atmosphere, the supernatant (4 ml) was replaced with fresh 0.01 $\underline{M}$ $CaCl_2$ containing no quinoline and then agitated for an additional 4 hr under N_2. Again, 4 ml of supernatant was removed, counted and replaced with fresh $CaCl_2$ solution and the process repeated. Radioactivity measurements at the end of each 4 hr incubation were used to generate the desorption curve. Kinetic experiments indicated that 4 hr was sufficient to achieve desorption equilibrium.

Competitive sorption experiments were conducted by performing the sorption experiments as described above with the addition of pyridine to give an initial pyridine concentration of 1 ppm, 5 ppm, or 10 ppm.

RESULTS AND DISCUSSION

The quinoline adsorption isotherms for each of the nine subsoils could be described by the Freundlich equation and gave good fits to the linear form of the equation:

$$\log S = \log K + {}^1/n \log C_s$$

where

$S = \mu$ moles quinoline per gram of soil

$C_s = \mu$ moles quinoline per ml of solution

The quinoline Freundlich constants and linear correlation coefficients are given in Table II.

Banwart et al. (1982) measured the sorption of two analogs of quinoline, namely, biquinoline and acridine, and found the sorption of these compounds in soils and sediment to correlate highly with the percentage of soil organic carbon. Interestingly, quinoline shows no correlation (r^2 = .0100) with the organic carbon content of subsoils used in these studies. Additionally, the correlation was not improved by considering alkali extractable organic carbon as is commonly observed for metal adsorption (Luoma and Bryan, 1981). An explanation for this behavior may be the relative hydrophobicity of the molecules. Quinoline has a water solubility of 6,000 ppm and a octanol/H_20 partition coefficient of approximately 107 (Verschueren, 1983). The water solubility of biquinoline and acridine are 1.02 ppm [illegible]d 38.4, respectively and their octanol/H_20 partition coefficients are 20,200 and 4,200, respectively. For the acridine and biquinoline hydrophobic bonding may be the predominant sorption mechanism, while for the more polar quinoline, ionic mechanisms become important. Another consideration is that of the 14 soils used by Banwart et al. (1982), only 2 soils had a pH below 6. In most of the soils studied, therefore, acridine and biquinoline exist in the neutral form and thus hydrophobic binding would be favored over ionic mechanisms.

The low organic carbon content of the subsoils in this study may also play an important role. While some investigators have found good correlation between adsorption of hydrophobic and halogenated compounds and organic carbon content in low organic carbon soil and subsoil (Banwart et al., 1982; Schwarzenbach and Westall, 1981; Wilson et al., 1981) others observe that the properties of the mineral fraction or pH become increasingly important when the compound is polar or ionizable (Khan et al., 1979; Zierath et al., 1980).

An examination of the Freundlich constants (Table II) and the physical properties of each soil (Table I) reveals that pH has a major influence on the sorption of quinoline with the acidic soils exhibiting the greatest sorption. In the acidic soils, quinoline (pKa = 4.90) is predominantly in the protonated form. This suggests a cationic ad-

Table I. Selected subsoil properties

Subsoil	% Organic Carbon	% Extractable Organic Carbon	% Clay	pH (H_2O)	pH (.01 M $CaCl_2$)
Elk	0.22	0.16	32.0	4.23	3.72
Dormont	0.26	0.19	37.0	4.63	4.26
Westmoreland	0.20	0.13	20.0	4.75	4.18
Loring	0.24	0.19	27.0	4.85	4.18
Ft. Martin	0.74	0.17	32.0	5.19	5.27
Vernita	0.02	0.038	1.0	7.16	6.88
Vebar	0.35	0.15	14.0	8.00	7.46
Anvil Pts.	0.58	0.16	28.0	8.15	7.64
Zahl	1.21	0.41	34.	8.17	7.70

Table II. Freundlich constants

Subsoil	K	$^1/n$	r^2	$^1/n = 0.7$ K	r^2
Elk	5.83	0.766	0.995	7.35	0.994
Dormont	3.18	0.656	0.999	3.56	0.998
Westmoreland	2.76	0.554	0.996	4.23	0.986
Loring	5.80	0.585	0.994	8.29	0.990
Ft. Martin	6.12	0.715	0.990	5.71	0.991
Vernita	0.411	0.614	0.993	0.518	0.975
Vebar	0.512	0.836	0.997	0.337	0.999
Anvil Pts.	1.13	0.907	0.999	0.655	0.993
Zahl	1.02	0.797	1.00	0.792	0.996

sorption mechanism as the major mode of quinoline binding. However, the Freundlich constants did not correlate with solution hydrogen ion concentration ($r^2 = 0.329$), even with K values from linearized Freudlich isotherms where $^1/n$ was forced to 0.7 (average $^1/n$ value for the 9 soils used). The Freundlich constants did not show a significant correlation with clay content ($r^2 = 0.280$) or surface area ($r^2 = 0.571$).

Though cation exchange capacity is likely an influencial parameter, calculations indicate that at maximum quinoline adsorption (e.q., in the Elk subsoil), only 0.41% of the cation exchange equivalents are balanced by quinoline, assuming presence of the protonated species. At such low surface coverage, surface charge density and other microscopic properties of the adsorbing surface are likely more important than a cation exchange capacity. The influence of surface charge density and 2:1 mineral structure on adsorption of certain organic cations is well established (Weed and Weber, 1969; Philan et al., 1970).

The presence of a cationic adsorption mechanism is further substantiated by the decrease in quinoline adsorption which occurs in acid subsoils in presence of increasing Ca^{+2} concentrations. Increasing Ca^{+2} from 0.001 M to 0.1 M significantly reduces quinoline adsorption (1.30 ppm initial concentration) when the subsoil pH is near or below the compound pKa. However, a more weakly exchanged univalent cation (K^+) has a lesser effect. The Freundlich adsorption constant in 0.01 M $CaCl_2$ is one-half that observed in distilled, deionized H_20 (Fig. 1). When the subsoil pH is significantly above the pKa of quinoline (e.g., pH >7.0), the effects of 0.01 M $CaCl_2$ are negligible as shown for the Anvil Points subsoil (Fig. 1). These results suggest that Ca^{+2} competes with positively charged quinoline species for cation exchange sites, though quinoline has higher surface specificity.

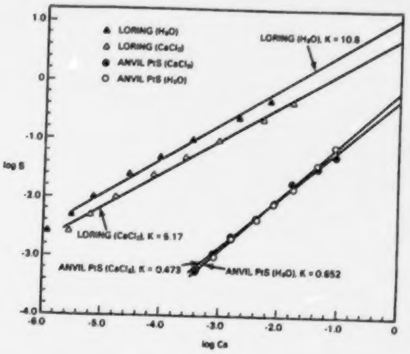

Figure 1. Freundlich Plots of Quinoline Sorption from Water and $CaCl_2$ (0.01 M) on Loring and Anvil Points Subsoils

Desorption

The desorption of quinoline (Fig. 2) was examined on an acidic (Loring, pH = 4.85) and a basic subsoil (Anvil Points, pH = 8.15). The desorption experiment was initiated at two different adsorbed concentrations of quinoline: 29.1 µg/g and 54.4 µg/g for the Loring, and 4.6 µg/g and 7.1µ g/g for the Anvil Points subsoil. These adsorbed concentrations result from equilibrations with initial solution concentrations of 6.5 µg/ml and 12.9 µg/ml. In both subsoils, desorption shows significant hysteresis, it is, however, more pronounced in the more adsorbent, acidic subsoil (Fig. 2). After 4 solution replacements (4 ml each), only 10.3% of the quinoline was desorbed at the lower subsoil concentration and 15.6% was desorbed at the higher concentration. In contrast, the Anvil Points subsoil exhibits significant reversibility with 57.2% desorption occurring at the low concentration and 60.3% at the high concentration.

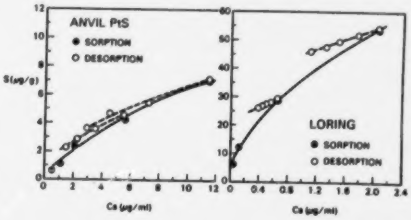

Figure 2. Desorption of Quinoline from Loring and Anvil Points Subsoils

The desorption behavior of quinoline compares favorably with that observed using layer lattice silicates as adsorbents. Adsorption reversibility at intermediate pH values is low on layer silicates and decreases with decreasing pH, suggesting strong retention of positively charged species (Doehler and Young, 1960; Helmy et al., 1983). Similarly, poor adsorption reversibility is also noted for other organic cations by smectites, though desorption occurs readily from vermiculite (Weed and Weber, 1969). The rapid desorbability of quinoline on the basic subsoil exceeds that observed for smectites at comparable pH and is further indication of the weak binding of the neutral species in these subsoils.

Competitive Sorption

Leachates from waste disposal sites commonly contain multiple organic components and competitive interactions between solutes may influence adsorption and transport. As a preliminary analysis of this phenomenon, the competitive effect of pyridine on the sorption of quinoline was examined. Pyridine is a single ring, basic nitrogen aromatic heterocycle found in energy wastes which is miscible in water and has an octanol/H_2O partition coefficient of 4.4. Pyridine has pKa of 5.25 at 25°C as compared to 4.90 at 20°C for quinoline (Weast and Astle, 1981).

The competitive experiments were conducted using an acidic (Loring) and basic subsoil (Anvil Points). In the basic subsoil, the effect of pyridine was negligible (Fig. 3). Both neutral solutes adsorb independently. This is not surprising since the sorption of pyridine in the basic subsoils is very low and it is not expected to be an effective competitive compound. At a ratio of 2 g soil to 10 ml solution (same as used for quinoline), the sorption of pyridine is hardly measureable.

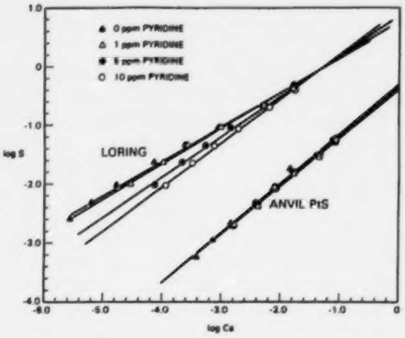

Figure 3. The Effect of Pyridine on Quinoline Freundlich Plots for Loring and Anvil Points Subsoils

In the acidic subsoil, pyridine sorption (Freudlich, K = 5.78; $1/n = 0.679$) is comparable to that of quinoline (K = 5.80, $1/n = 0.585$) and was expected to compete very effectively for quinoline binding sites. Surprisingly, the effect of pyridine on quinoline sorption was not very pronounced (Fig. 3) suggesting an excess of available adsorption sites. As might be expected, the maximum effect of pyridine was seen at low initial quinoline concentrations. At an initial concentration of quinoline of .250μg/ml, the addition of 10 μg/ml pyridine reduced quinoline sorption by 4.5%; at an initial quinoline concentration of 12.9 μg/ml, a 3% reduction in sorption was observed.

An interesting feature of the competitive Freundlich plots is the fact that they converge at higher equilibrium concentration and suggest a cooperative effect of pyrdine on quinoline sorption. If the Freundlich plots in Fig. 3 are valid at high quinoline concentrations, the presence of pyridine should increase quinoline sorption. Experiments to verify this observation are presently underway.

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CHARACTERIZATION OF SOIL ORGANIC MATTER USING INSTRUMENTAL METHODS

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ABSTRACT

It is generally implied that for hydrophobic pollutants soil organic matter, clay minerals and possibly amorphous hydroxides are the primary earth materials that influence the attenuation of organic pollutants in the subsurface environment. One of the primary objectives of our present research is to establish the distribution of these materials both vertically and areally and to obtain quantitative estimates of these compounds in a wide number of samples. Scanning electron microscopy is a common method of characterizing clay minerals from the deeper subsurface, but the dehydration of soil organic matter in soils without destroying their structure is difficult at best and probably will require special freeze drying equipment. Quantitative x-ray diffraction, a viable method for simple mixtures of well crystalline compounds, becomes at best semi-quantitative for multicomponent mixtures, and next to useless for amorphous or poorly crystalline materials such as some clays, natural organic matter and amorphous hydroxides. Fourier Transform Infrared Spectrometry although used extensively to characterize extracted humic and fulvic acids lacks the sensitivity to detect the much smaller amounts present in unextracted soil samples. Raman microprobe techniques can yield molecular bond information that is not obtainable by conventional techniques. Information on the molecular nature of the components of a sample, the distribution in the sample, and the chemical and physical character of the matrix are characteristics that may be explored.

INTRODUCTION

Because the materials being studied are some of the most complex in nature and because of the difficulty of determining the behavior of pollutants in contact with soil, the soil and its components must be characterized, or at least catagorized. The inorganic parts consist of clays, amorphous hydroxides and oxides. The organic fraction, on the other hand, is composed of literally millions of complex organic compounds generated from the chemical and biological degradation of plant and animal residues. These compounds are known collectively as soil organic matter (50M), or humic substances.

These inorganic and organic fractions can form complexes with each other, and with toxic wastes (both organic and inorganic) and thus they affect the transportation, concentration and distribution of any toxic materials in contact with them.

INSTRUMENTAL METHODS

The instrumental techniques utilized in this study have been scanning electron microscopy (SEM) to observe the shapes and distributions of soil constituents, including SOM; x-ray diffraction for the qualitative and quantitative analysis of the crystalline soil constituents; Fourier Transform Infrared Spectroscopy (FTIR) and Raman Microprobe, for the molecular bond characterization of soil constituents.

Scanning Electron Microscopy

Numerous researchers have studied various aspects of soil formation, micromorphology, and mineralogy using the SEM, but few have included an examination of soil organic matter.

The examination of soil using scanning electron microscopy without some type of freeze drying invariably leads to spattering when probed by an electron beam. No obvious organic structures were observed after rapid cooling in liquid nitrogen followed by freeze drying. The only technique not tried that seems feasible is that advocated by Gilliott (1969) who used a quick-freeze followed by freeze-drying at less than −130 C as the most effective method for preserving the original soil structure without creating ice artifacts on the sample. The drawbacks to this technique are that it is a very slow process, and that it would involve the purchase of some expensive state-of-the-art equipment.

X-Ray Diffraction

Powder x-ray diffraction analysis is an excellent technique for the quantitative analysis of simple crystalline-mixtures. The intensity of each component's pattern is proportional to the amount present, when corrected for absorption. If a mixture contains both a weak absorber and a strong absorber the signal due to the weak absorber will be attenuated, while the peaks of the strong absorber will be even further enhanced over those of the pure unmixed samples, even if those are run under identical conditions. The method used for quantitative x-ray diffraction analysis is the one developed by Hooton and Giorgetta (1977) who assume that a constant for an instrument with a given configuration and with a constant Beam intensity can be determined for each mineral. If it is assumed that the sum of the weight fractions is equal to 100% then it is possible to determine weight fractions of individual components, without references to calibration curves and mixing standards. An easy method to determine relative values of H is to select one mineral as a reference standard, assign a value to H for that mineral, and determine H for all other minerals by mixing them in known proportion with the standard and using the appropriate equations.

Quantitative x-ray diffraction using an external standard system requires extreme machine stability and the availability of pure samples of all the constituents. This is not the case when one is dealing with mixed layer clays, or those that are not perfectly crystalline. This unfortunately is the usual case with soil clays. The final limitation is the presence of amorphous constituents in the sample, especially those like amorphous oxides and hydroxides of iron and manganese which are particularly strong absorbers, and which in addition give rise to fluorescence effects.

Spectrometry

Whereas X-ray diffraction is a result of the total crystal structure, infrared spectroscopy looks at individual bonds, making it one of the few tools available for characterizing amorphous constituents such as natural organic matter, amorphous hydroxides and synthetic organic pollutants.

Fourier Transform Infrared Spectrometry -FTIR

A recent development of infrared spectroscopy is the availability of Fourier Transform Infrared Spectroscopy (FTIR) which has higher sensitivity than the older wavelength instruments as well as having computerized data manipulation capabilities including spectral stripping. The latter is essentially the non-chemical separation of mixtures using difference or subtraction spectroscopy.

Common FTIR instrumental configurations are simple specular reflectance, attenuated total reflectance (Harrick, 1981), photoacoustics (Rockley, 1980), diffuse reflectance and transmission methods.

The spectral reflectance or attenuated total reflectance method although very fast was prone to severe absorption effects that dramatically distorted the spectral peaks (Christiansen effect); the photoacoustic detector lacked the sensitivity essential for the concentrations we were seeking and required too long a purging time; the diffuse reflectance method required too great a dilution such that the resulting sensitivity was inadequate for our purpose. Standard transmission FTIR techniques using pressed KBr pellets were tried and high quality spectra were obtained in a relatively short time, primarily determined by the sample preparation time. Given all the previous considerations, this measurement technique is probably the optimum choice. Major problems with this method in general are the presence of moisture in the samples, and the lack of sensitivity of the technique to detect natural organic matter in amounts less than about 1%. We also concluded that the examination of clay-SOM-organic-pollutant complexes will require separation and concentration of the various humic and fulvic acids and that the spectroscopic measurement of chemical bonds formed between pollutants and the substrate, necessary to define the mechanism for chemical adsorption from ground waters, will be tedious and difficult with a low probability of success.

Laser Raman Microprobe

The most recent addition to the study is the Raman Laser Microprobe, which is ideally suited to the examination of particulates (Delheye, 1979), and we anticipate the organic and inorganic constituents of soil. Major advantages of the Raman method (Grasselli, 1981) are that it is nondestructive and requires little sample preparation time. Sample may be analyzed in situ. It is molecularly specific, and samples may include all states of matter, and thus any type of molecule organic, inorganic, or biological (Tu, 1982) may be identified. Further, it does not require the use of a vacuum or other type of sample pretreatment. One final advantage is that water, which is a major limitation of Infrared technique, exhibits only a very small Raman signal, and it does not matter if the sample contains or is examined in water. Major limitations of the Raman method are the inherent weakness of the Raman effect, the weak signals being difficult to detect and thus placing strenuous requirements on the spectrometer. Local heating effects caused by a buildup of heat in the sample from the laser radiation may exist, although examining the sample in water or by reduced laser beam intensity may ameliorate this problem. The weak Raman signal may be difficult to detect when the sample also emits flourescence. Using a quenching technique may eliminate the problem. Finally lack of standard reference spectra (because of the newness of the analytical technique) makes identification of unknowns more time consuming.

The Laser Raman Microprobe has been in use only a limited time and we have not as yet been able to carry out many of the investigations we hope to do. At this point we have made an effort to characterize some of the standard clays, including montmorillonite and several Kaolinites. In time, we hope to be able to identify an adsorbed organic pollutant and to determine whether its substrate is an organic or inorganic fraction of the soil. Our immediate objective is to the mode of distribution of the natural organic matter in the various soil types. The ultimate limits of detection, quantitation of individual species present, sample size, sample heating and fluorescence, and the compositional complexity of sample are questions whose answers must wait for increased understanding that will come from future studies.

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SORPTION KINETICS OF TOXIC AND HAZARDOUS ORGANIC SUBSTANCES ON NEW JERSEY COASTAL PLAIN AQUIFER SOLIDS

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ABSTRACT

Studies examining the sorptive characteristics of selected organic pollutants to representative soil samples from New Jersey aquifers are described. The soil from the Cohansey aquifer is a sand with a small organic fraction. Equilibrium studies examining lindane exhibited a linear adsorption isotherm with an association constant of 0.013 l/g. Desorption isotherms indicated a pronounced hysteresis, indicating that the sorption process for this system is not completely reversible.

INTRODUCTION

The USGS (1981) recently identified that 19% of wells sampled in the Potomac-Raritan-Magothy Aquifer system, shown in Fig. 1, contained detectable concentrations of nine volatile organic compounds including chloroform, benzene, 1,1,2-trichloroethane, and trichloroethylene. This aquifer system presently accounts for greater than half the current groundwater pumpage in the New Jersey coastal plain. Pollution problems are not just limited to this system as the Cohansey and Kirkwood formations, also shown in Fig. 1, are subject to contamination from overlying landfills.

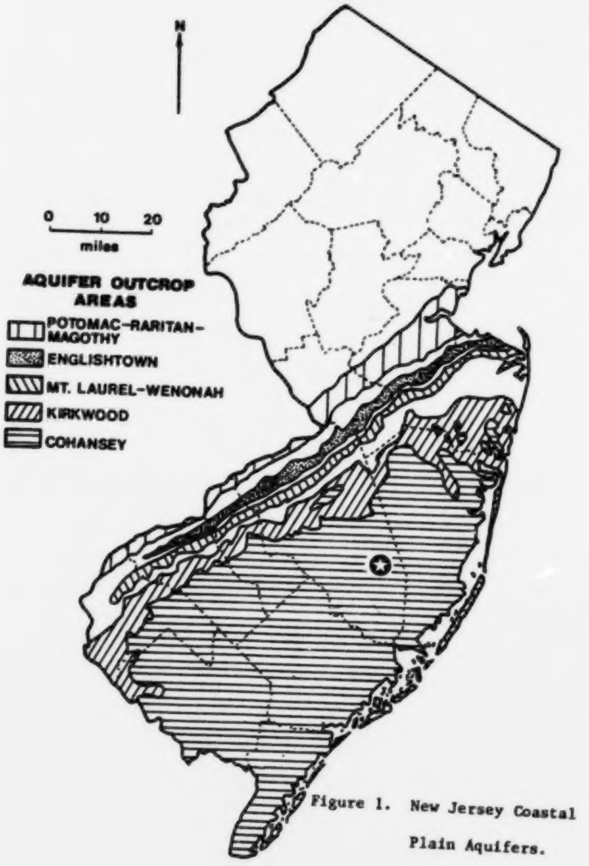

Figure 1. New Jersey Coastal Plain Aquifers.

Mathematical models of pollutants in porous media all include a reaction term to account for not only the chemical and biochemical reactions but also sorption kinetics (Uchrin, 1983). Certain organic substances tend to be rather non-reactive but are hydrophobic and thus associate quite strongly to solid particulates. Other substances can be strongly attracted to functional groups which may be present on the solids. Knowledge of a pollutant's sorptive characteristics in a particular solvent-adsorber system is critical to prediction of its transport and ultimate fate in groundwater systems.

The Environmental Science Department, Cook College, Rutgers University, is currently performing research for determining the sorptive kinetic characteristics of several pollutants known to exist in New Jersey groundwater to representative solids from the State's aquifers. Experiments are being performed in two modes. Batch studies are being conducted to determine the net rates of adsorption, the time by which equilibrium is reached, and finally the resultant equilibrium distribution of the pollutant in the solid and liquid phases. Desorption equilibrium studies are also being performed. Subsequent to the batch studies, flow-through column studies will be performed. This paper will describe the methodology being employed for the batch experiments as well as some preliminary results examining the sorptive characteristics of lindane to the Cohansey aquifer solids.

SOIL CHARACTERISTICS

The soil used in this study was taken from a location at the Rutgers University Cranberry Culture Experiment Station near Chatsworth, NJ. The location is shown as the star in Fig. 1 and is in the Cohansey aquifer outcrop area. The specific site had no prior history of cultivation and the organic top layer had recently been scraped in preparation for cultivation.

A sieve analysis showed the soil to be predominately sand, ranging from very fine to very coarse. Further mechanical analyses showed that the soil is comprised of 90% sand, 8% silt, and 2% clay. The organic content was found to be 4.4%. A grain size distribution is displayed in Fig. 2.

SOLUTE CHARACTERISTICS

Lindane was selected for examination due to its little if no tendency to biodegrade (Patterson and Kodukala, 1981), its relatively low volatility, its historical use as a pesticide in the Mid-Atlantic region, and the

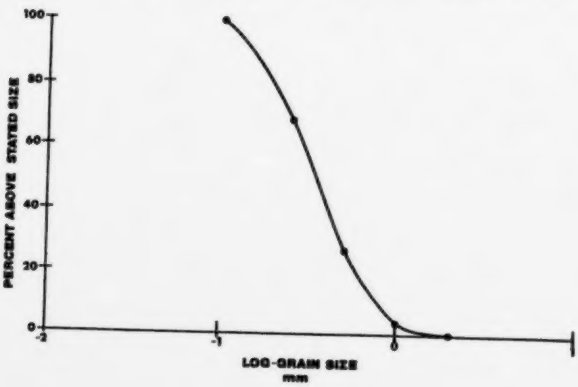

Figure 2. Grain Size Distribution - Cohansey Aquifer Soil.

existence of past studies including Kay and Elrick (1967), Mills and Biggar (1969), Ehlers, *et al.* (1969a & b), Spencer and Cliath (1970), and Huggenberger, *et al.*,(1972).

EXPERIMENTAL PROCEDURE AND RESULTS

Rate Studies

Batch rate studies were performed by first air drying the soil. A predetermined mass of soil was then introduced into a series of 50-ml screw cap culture tubes. One tube was kept empty as a blank. The soil was then saturated with 0.5-5.0-ml of organic-free water. The tubes were then spiked with a 30-ml volume of a solution of lindane in water. A carrier solvent was not used. The tubes were immediately sealed by screwing on teflon-lined caps and agitated by wrist shakers. Tubes were withdrawn at intervals of 1, 2, 4, 8, 24, 48, and 78 hours for analysis.

To determine the residual concentration, the tubes were centrifuged to separate the solids. The centrifugate was then carefully decanted and diluted as appropriate. A 5-ml volume sample was then withdrawn from each vial and extracted with 5-ml of pesticide-grade hexane and the extract analyzed using a Hewlett-Packard 5840-A gas chromatograph. The resultant equilibrium concentration versus time plot for lindane on the Cohansey soil, displayed in Fig. 3, shows that equilibrium was essentially reached for this system by 24-hours. Analysis of the blank showed loss to the glassware to be negligable (less than analytical error).

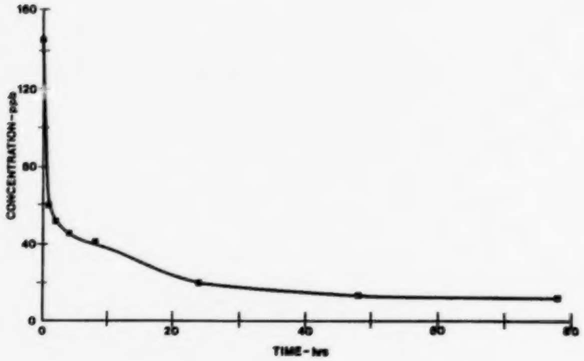

Figure 3. Rate of Adsorption of Lindane to Cohansey Aquifer Soil.

Adsorption Equilibrium Studies

An identical procedure to the rate studies was employed except that a matrix consisting of different pollutant spike concentrations as well as different soil masses was examined and the agitation by wrist shakers was carried out until equilibrium was reached. A Freundlich Isotherm was first fitted to the data and yielded a slope of near unity, which suggested a linear relationship. A linear isotherm, shown in Fig. 4, was then fitted to the data and exhibited a close correlation (r = 0.97). The slope of the fitted linear isotherm was computed to be 0.013 l/g. This value is similar to the value (0.010 l/g) found by Kay and Elrick (1967) for sand with organic matter.

Consecutive Desorption Equilibrium Studies

Some of the centrifuged solids obtained from the equilibrium adsorption studies were immediately subjected to consecutive desorption analyses. The liquid centrifugate was carefully drained from the culture tubes and replaced with 30-ml of organic free water. The tubes were then sealed with the teflon-lined screw tops and agitated for 24-hours. The tubes were then withdrawn, centrifuged, and the centrifugate analyzed as before. This procedure was performed four more times. Results of these analyses, shown in Fig. 4, evidence a pronounced degree of hysteresis, suggesting that the adsorptive and desorptive processes are not completely reversible. These results are consonant with results of other investigators, including van Genuchten, *et al.* (1974) and DiToro and Horzempa (1982), examining similar organic solute/adsorber systems.

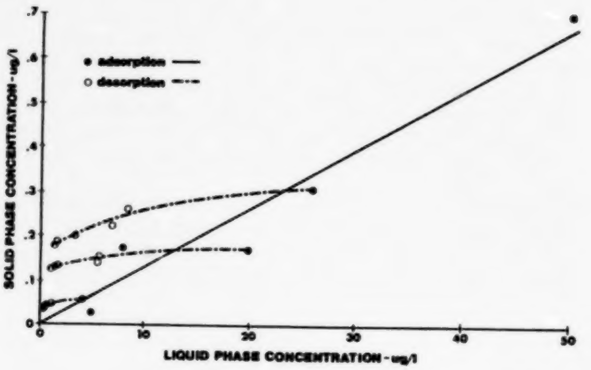

Figure 4. Sorption Isotherms for Lindane to Cohansey Aquifer.

Column Studies

Column studies have been designed and the column apparatus is currently under construction. The systems will be operated in the saturated mode and will be closed to minimize volatilization. Results from the batch studies will be used to design flow rates and bed depths. Eventually the data from both the batch and column studies will be incorporated into a mathematical model.

SUMMARY

The problem of characterizing the behavior of hydrophobic organic pollutants in groundwater systems is complex. Investigators at the Department of Environmental Science, Rutgers University, are currently conducting an integrated research effort involving laboratory studies aimed at examining the characteristics of both adsorption and desorption of organic pollutants to groundwater solids in both static (batch) and flow-through (column) systems. The overall research effort should represent a significant advance in developing a better understanding of the processes involved in the transport and behavior of organic pollutants in groundwater systems.

ACKNOWLEDGEMENTS

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EVALUATION OF PARTITIONING PROCESSES FOR ORGANIC CONTAMINANTS IN GROUND WATER

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ABSTRACT

Extensive contamination of the ground water resources of the U.S. by organic pollutants has precipitated a need to evaluate the movement and fate of these substances. This, in turn, has led to the development of models for simulating contaminant transport and transformation processes in ground water systems. One of the most important of these processes for organic contaminants is sorption on aquifer soils.

Sorption is a dominant process for many organic solute-soil systems, one which may retard the movement of the solute to a rate which is orders of magnitude less than that of the water itself. Accurate description of sorption less than that of the water itself. Accurate description of sorption is a requisite for transport analysis in such systems. Description of sorption processes must include the characterization of equilibrium, the approach to equilibrium and sorptive hysteresis which may occur in the sorption-desorption of organic solutes in ground waters.

INTRODUCTION

Extensive ground water contamination by persistent organic pollutants has occurred over the past two decades. The desire to manage and evaluate existing ground water contamination and design safe methods of disposal for possible contaminants has led to a need for more precise methods of assessing the transport and fate of organic contaminants in ground waters. These assessments must be based upon identification, description and quantification of the significant transport and transformation processes operative in a given system. Processes of most frequent concern include mean bulk fluid movement, fluid dispersion, inputs and outputs by and to contaminant sources and sinks, sorption and chemical and biological transformation processes. The purpose of this discussion is to present a brief overview of the process of sorption, and of the factors which impact this process. This overview will include consideration of sorption equilibria, sorption kinetics and desorption.

BACKGROUND

The movement of a contaminant in a ground water system is governed by the hydrodynamic properties of the flow system and such transformations as are operative. These relationships may be written in a general equation form (Bear, 1979)

$$\frac{\partial C}{\partial t} = \mathrm{div}(D_h \cdot \mathrm{grad}\ C) - v \cdot \mathrm{grad}\ C - \rho \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{rxn} \qquad (1)$$

where:

C = liquid phase concentration of solute (M/L^3);
t = time (t);
D_h = hydrodynamic dispersion coefficient (L^2/t);
v = interstitial fluid velocity (L/t);
ρ = solid phase particle density (M/L^3);
ϵ = volumetric fraction represented by the liquid phase (L^3/L^3);
q = normalized solid phase concentration of sorbed solute species (M/M); and
rxn = subscript denoting biological or chemical reaction of the solute in the solution phase.

Sorption is represented by the third term on the right hand side of equation 1. In detailing the sorption subsystem equations it is necessary to evaluate the behavior of the solid phase concentration (q) as a function of the liquid phase concentration (C), solute properties, solid phase properties, and time. Laboratory methods employing either completely mixed batch reactors (CMBR's) or plug flow reactors (PFR's) may be utilized for such subsystem detailing. In a CMBR the contents are well mixed and assumed uniform, eliminating the role of velocity and dispersion. Thus,

$$\left(\frac{\partial C}{\partial t}\right)_{CMBR} = f(V,M,C) \qquad (2)$$

where:

V = volume of solution phase (L^3); and
M = mass of solid phase (M)

The general expression for a PFR reactor is derived from equation 1 and may be given, in one-dimensional form and considering only the sorption reaction, as:

$$\left(\frac{\partial C}{\partial t}\right)_{PFR} = D_h \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \rho \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} \qquad (3)$$

where:

z = one dimensional spatial variable (L).

METHODS AND MATERIALS

Both CMBR and PFR methodologies have been employed to collect data for a matrix of aquifer sands and the organic solute lindane. Reactor configurations included CMBR's of both the tumbled-bottle and stirred type, and PFR's consisting of packed beds. The properties of the soils and solute used are summarized in Tables I and II. Experiments have been performed to characterize and quantify both sorption/desorption equilibria and kinetics.

TABLE 1

Soil Properties

Physical/Chemical Parameter	Ann Arbor Soil	Delta Soil	Michawye Soil	Portage Soil
Median Grain Size	.232 mm	.321 mm	.432 mm	.393 mm
Grain Size Uniformity Coefficient (d_{60}/d_{10})	2.616	3.098	2.462	2.500
Hydraulic Conductivity Coefficient	4.15×10^{-3} cm/sec	1.18×10^{-3} cm/sec	1.10×10^{-3} cm/sec	2.60×10^{-3} cm/sec
Total Organic Carbon Content	1.14%	.12%	.38%	.10%
Cation Exchange Capacity	6.9 meq/100gr	5.0 meq/100gr	7.0 meq/100gr	7.0 meq/100gr

TABLE II

Lindane Properties

LOG K_{ow}	=	3.72
Henry's Constant	=	2.4×10^{-7} M^3/ATM.MOL
Aqueous Solubility	=	7.2 ppm

ASPECTS OF SORPTION MODELING

The "retardation" approach is a common technique for modeling sorption in ground water systems (Anderson, 1979). The foundations of this approach are the assumptions that sorption is a linear function of solution concentration, that sorption equilibrium is obtained immediately, and that sorption is a thermodynamically reversible reaction described by the sorption isotherm. Application of these assumptions provides a simplified and convenient form for mathematically describing transport of a sorbing solute. The retardation approach describes the movement of a sorbing organic contaminant concentration front identical in shape to that of a conservative contaminant but delayed in time. The assumptions yielding the retardation equation are not universally applicable. The following discussion summarizes aspects of sorption which must be considered for cases in which the retardation modeling approach is inappropriate, and presents representative results from laboratory studies.

SORPTION EQUILIBRIA

Sorption equilibria were evaluated using CMBR bottle point methods to obtain data relative to the relationship between solid phase solute concentration and liquid phase solute concentration at a given temperature. This relationship is termed a sorption isotherm. An overlay of sorption isotherms for lindane and the four soils tested is presented in Figure 1. These isotherms were observed to be nonlinear over the concentration ranges studied. As indicated in Figure 1, they could be linearized by plotting on a log-log scale suggesting that the Freundlich model provides a good approximation of observed equilibrium behavior. The Freundlich model has the following form (Weber, 1972):

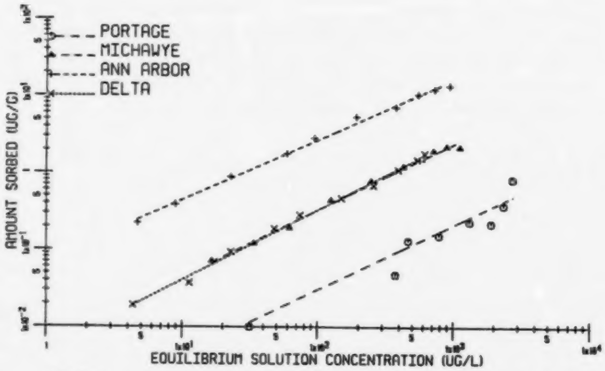

FIGURE 1. FREUNDLICH SORPTION MODEL SOIL COMPARISON
RUN 2 PORTAGE 2:1 RUN 4 MICHAWYE 1:2
RUN 6 ANN ARBOR 1:5 RUN 9 DELTA 2:1

$$q_e = K_f C_e^{\,n}$$

where:

q_e = normalized solid phase concentration at equilibrium (M/M);
C_e = solution phase concentration at equilibrium (M/L³);
K_f = constant related to sorption capacity; and
n = constant related to sorption intensity.

The value of the exponent for a Freundlich isotherm is a measure of its linearity or nonlinearity, with convex or concave isotherms resulting for exponents greater than or less than one, respectively. The mean exponent observed for sorption of lindane by the four test soils was 0.82, yielding a nonlinear concave isotherm. This is not the first report of nonlinearity for sorption of organic solutes by soils. Hamaker and Thompson (1972) summarized a large volume of literature pertaining to a variety of solids and organic solutes and concluded that sorption isotherms are frequently nonlinear, with exponents typically less than unity.

SORPTION KINETICS

The kinetics of sorption were investigated in both CMBR and PFR experimental systems. The results of these investigations indicate that sorption of lindane by the four test sands is a time dependent phenomenon characterized by a rapid initial rate and followed by a slower sustained rate requiring several days to approach equilibrium. Figures 2 and 3 present typical rate data for CMBR bottle-point and stirred reactors, respectively.

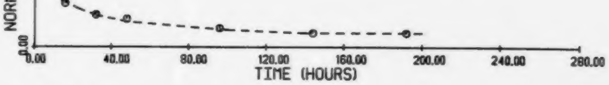

FIGURE 2. BOTTLE POINT KINETICS
RUN NO. 9 1:2 SOIL:SOLUTION
Co=590.1 ug/l LINDANE ANN ARBOR SOIL

Figure 3 also depicts the results of efforts to model the kinetics of sorption using a variety of classical sorption modeling approaches, including: first-order kinetics, first-order kinetics with an instantaneous component, second-order kinetics, and the dual-resistance approach of the Michigan Adsorption Design and Applications Model (MADAM). The details of these modeling methods are presented elsewhere (Miller and Weber, 1984). Of the four models investigated the MADAM model provided the closest approximation to the observed kinetic behavior.

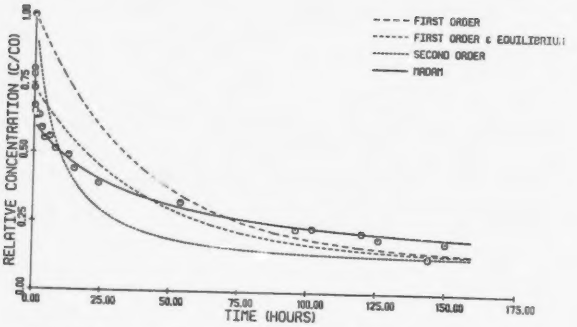

FIGURE 3. STIRRED BATCH KINETIC REACTOR
RUN 8 ANN ARBOR-LINDANE SOLIDS:SOLUTION 1:10

Figure 4 represents a typical PFR breakthrough curve for lindane and the Ann Arbor soil. The trend is a more rapid initial breakthrough and a slower approach to equilibrium than would be predicted by retardation modeling. The variety of kinetic models applied to batch systems may also be applied to PFR modeling by appropriate inclusion of the hydrodynamic terms advection and dispersion.

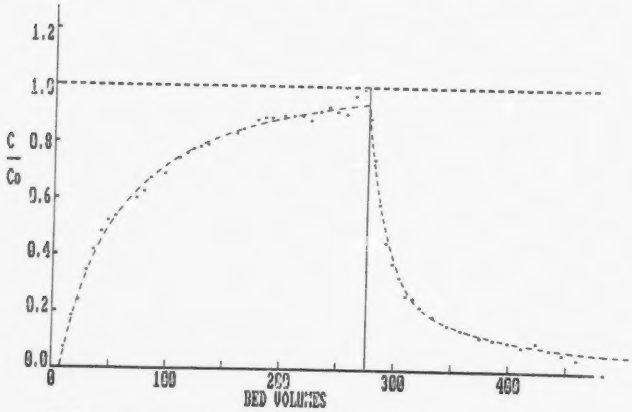

FIGURE 4. BREAKTHROUGH CURVE FOR ANN ARBOR SOIL - LINDANE RUN 6

DESORPTION

Other investigators (van Genuchten et al, 1974, and DiToro and Horzempa, 1982), have reported that desorption is hysteretic and not completely reversible. Similar conclusions have been reached from this study for both CMBR and PFR experiments. Figure 4 presents a typical pattern of desorption in a PFR system. Integration of the entire sorption-desorption curve indicates that a portion of solute remains on the solid phase. This finding was confirmed by extraction of the soil after elutriation with an organic free aqueous solution yielded no additional removal of lindane from the soil. Similar results have been encountered for CMBR isotherms which substantiate the hysteretic nature of desorption. The degree of reversibility appears directly related to the organic content of the soil and the amount of time elapsed at an equilibrium condition (aging time) prior to desorption, but more data is required to fully elucidate this trend.

CONCLUSIONS

The present investigations suggest that the sorption of organic solutes in ground water systems is a complex process involving nonlinear and hysteretic equilibrium behavior and a relatively slow rate of approach to equilibrium, at least for the systems studies. These factors suggest that a more detailed and complete description of the sorption process may improve predictive methods for assessing the fate and transport of organic solutes in ground waters.

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GROUNDWATER CONTAMINATION AT CONROE WASTE DISPOSAL SITE

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ABSTRACT

Ground water contamination at the Conroe waste site has been investigated for the past two years. The concentrations of trace level organics (TLOs), inorganics, and metals in ground water were analyzed. Major organic constituents detected were polynuclear aromatic hydrocarbons, phenolics, and nitrogen- and sulfur-heterocyclic compounds. Depth to water, conductivity, chloride, pH, and dissolved oxygen were monitored to indicate possible degradation and migration of contaminants in ground water.

Various water sampling, laboratory procedures, and GC identification methods for TLOs were evaluated. A Teflon bailer was used in water sampling for its rigidity and inertness. Sep-Pak extraction procedures have the advantages of simplicity and versatility in the sample preparation and have shown better reliability and less cross contamination than conventional liquid-liquid extraction procedures. The reproducibility and recovery efficiency of fourteen target organic compounds selected in this study were from good to excellent.

Leaching of TLOs from soil into ground water was examined. The results indicate that the amount of TLOs absorbed by soil was significantly higher than the amount leached into ground water. The major organic compounds found in the water soluble fraction of Conroe pit soil were pentachlorophenol and higher molecular weight alkanes. Based on the analytical data and overall variation of results due to field sampling, extraction procedure, and GC analysis, we conclude that the concentrations of TLOs in ground water have remained unchanged for the past two years.

INTRODUCTION

Trace level organics (TLO's) contamination of ground water at the Conroe waste site has been studied for the past two years. The water depth, conductivity, chloride, pH, and dissolved oxygen were monitored to study possible variation of contamination in ground water. Water soluble fractions (WSF) of Conroe pit soil were analyzed to determine possible TLO's input from contaminated soil.

Field sampling, laboratory extraction procedures and GC identification method were evaluated and standardized to quantitatively determine the changes of TLO's in ground water. A new Sep-Pak C_{18} procedure to enrich and extract TLO's was also examined to simplify and improve the field sampling and laboratory extraction procedure.

EXPERIMENTAL PROCEDURES

Glass and teflon bailers were used to sample wells 25-30 ft deep. About 2-5 well volumes were pumped before samples were taken.

In-day and between-day precision studies were performed on Well #2. A five consecutive-day sampling was started on Feb. 21, 1983, for a between-day sampling precision study. Two consecutive one liter samples were collected with a glass bailer after 30 liters of well water was pumped. Five consecutive one-liter samples were collected by the same procedure for the in-day precision study on Feb. 22, 1983.

Samples were extracted by liquid-liquid extraction or Sep-Pak C_{18} cartridges (Waters) in diethyl ether or methylene chloride.

Extracts were dried over anhydrous Na_2SO_4 and collected in concentrators. The extract was concentrated down to approximately 3 ml with a Vigreaux column over a steam bath. Final concentration to 0.1 ml was done with a stream of zero grade nitrogen.

The analyses were performed with a Tracor 560 gas chromatograph using packed or capillary column and FID detector. SP124ODA packed columns (6 ft long, 2 mm I.D.) were used for all the analyses performed before March 1983. Packed column helium carrier gas flow was 30 ml/min. Detector was set at 180°C and injector was 150°C. The temperature program was 50° for 4 min., increasing 8° per min to 180°C. 3 μl injection size was used.

A SGE DB-5 capillary (25 m long, 0.2 mm I.D., 0.25 μm film thickness) has been used since April 1983. Helium carrier gas flow was 1.7 ml/min, and the injection size was 1 μl. Detector temperature was 300°C, and injector was 250°C. Temperature program was 50°C for 4 min., increasing 8°C per min to 280°C. Identity of isolated products was verified by chromatography with authentic standards and by comparing mass spectral fragmentation patterns.

At the Conroe well site, water depths were measured with an engineer's steel tape. A YSI Model 33 was used to measure conductivity. A Hach Kit (Model #DR-EL4) was used to measure total chloride by the mercuric nitrate method. pH was measured in the field with litmus paper and a portable Hatch digital pH meter, and remeasured in the lab with a Corning pH meter (model #130).

To measure dissolved oxygen (D.O.) well casings were purged with zero grade Argon (Big Three Company, Houston, Texas) and water was pumped out with four or five peristaltic pumps. D.O. was monitored in each well with a YSI model 57 oxygen meter.

Water Soluble Fraction Conroe Pit Soil

A one liter sample of soil from the Conroe, Texas, creosote site was collected in the most contaminated zone (effluent pit area) with a solvent cleaned auger.

A 200 g sample of pooled soil was ground with a mortar and pestle for 10 min. and mixed with a metal spatula. Three 50 g soil samples were taken from the pooled soil and put in three 500 ml ground glass erlenmeyer flask filled with 200 ml of Silver Seal distilled water. Solutions were stirred for 24 hrs on magnetic stirrers, then allowed to settle. Liquid was poured off into centrifuge tubes and spun at 6500 x g (Sorvall superspeed RC2-B) for 30 min. Liquid was decanted and centrifuged again to get a clear, particulate-free liquid. Each sample was passed through a Sep-Pak cartridge and eluted with 4.5 ml methylene chloride. Sodium sulfate was used for drying when needed. Samples were concentrated to 0.2 ml under a stream of zero grade nitrogen. A blank without soil added was run through the entire procedure. The samples were analyzed using capillary G.C.

RESULTS AND CONCLUSIONS

TLO's contamination of ground water in Conroe creosote waste disposal site has been studied for the past two years. Water depths, conductivity, chloride concentration, pH, and dissolved oxygen measurement were determined and studied by our laboratory.

The overall variation due to well water sampling, laboratory extraction procedures, and GC identification method, was evaluated. The in-day and between-day precision studies were performed in March, 1983 (Table 1). The range of percent coefficient of variance (% C.V.) for in-day precision is 6.49 to 45.50 for 12 organic compounds and between-day is 13.65 to 49.31.

A capillary GC method has been used to re-analyze Well #1 and #2 samples from sealed capillary tubes stored in a freezer (−20°C) in June 1983. Improved efficiency and separation were achieved by using these analyses. The results are summarized in Table 2. The TLO's in the ground water have remained unchanged based on the C.V. of field sampling, extraction procedure, and GC analysis.

Table 1

Precision Study of Sampling and Extraction Procedures
(Conroe Well #2, March 1983)

	In Day Study				Between-Day Study	
	Packed Column GC Analysis (n=5)		Capillary GC Analysis (n=2)		Packed Column GC Analysis (n=10)	
	Concentration (ppb)	% C.V.	Concentration (ppb)	% C.V.	Concentration (ppb)	% C.V.
Naphthalene	817.1 ± 53.0	6.49	926.4 ± 37.1	4	815.0 ± 111.3	13.66
2-Methylnaphthalene	408.0 ± 70.7	17.33	440.6 ± 46.2	10	390.8 ± 128.3	32.83
1-Methylnaphthalene	176.8 ± 35.8	20.25	180.7 ± 24.6	14	177.4 ± 75.3	42.45
1,7-Dimethylnaphthalene	65.1 ± 25.0	38.40	48.8 ± 12.4	25	60.0 ± 13.6	22.6
Dibenzofuran	156.9 ± 26.3	16.76	145.3 ± 4.3	3	164.0 ± 54.9	33.48
Fluorene	101.7 ± 15.1	14.85	110.5 ± 1.8	2	100.9 ± 28.0	27.75
Anthracene	155.9 ± 53.3	34.19	168.6 ± 10.07	6	166.7 ± 82.2	49.31
Phenol	20.0 ± 9.1	45.50	8.2 ± 0.36	4	19.8 ± 6.6	33.33
2,4-Dichlorophenol	34.9 ± 5.8	16.62	50.8 ± 9.3	18	40.1 ± 11.5	28.68

1. Packed Column Analyses
   A. Range of % C.V. for In-Day Precision: 6.49 - 45.50 (5 replicate samples)

   B. Range of % C.V. for Between-Day Precision: 13.65 - 49.31 (2 replicate samples per day for five-day study)

2. Capillary Column Analysis
   A. Range of % C.V. for In-Day Precision: 2 - 25 (2 replicate samples)

Table 2

Organic Compounds Identified by Capillary GC (Conroe Wells #1 and #2)*
(Concentration in ppb)

	Well #1					Well #2				
	10/81	2/82	3/82	5/82	3/83	10/81	11/81	2/82	5/82	3/83
Naphthalene	19.6	41.5	30.2	39.0	59.0	359.6	497.2†	255.9	362.0	926.4
2-Methyl-naphthalene	1.4	7.1	4.8	10.6	12.0	191.6	228.3†	158.2	217.8	440.6
1-Methyl-naphthalene	6.2	3.0	2.3	4.5	5.0	105.2	169.5†	81.8	138.8	180.7
1,7-Dimethyl-naphthalene	ND	ND	ND	0.7	ND	7.7	20.9	10.0	21.5	48.8
Dibenzofuran	ND	0.9	1.2	5.0	ND	52.5	122.5†	91.3	167.5	145.3
Fluorene	ND	0.7	0.8	3.9	ND	31.6	85.7†	89.6	138.9	110.5
Dibenzothiophene	ND	ND	ND	1.5	ND	1.9	17.5	8.6	19.3	ND
Anthracene	ND	ND	ND	ND	ND	31.1	90.4†	139.2	18.0	168.6
Phenol	ND	ND	ND	0.9	ND	3.5	18.4	ND	1.6	8.2
2,4-Dichlorophenol	ND	3.8	ND	3.2	ND	54.4	ND	33.1	79.7	50.8
2,4,6-Trichloro-phenol	ND	ND	ND	ND	ND	63.5	ND	75.8	134.7	ND
m-Nitrophenol	ND	ND	ND	ND	ND	9.7	ND	43.0	34.9	ND
Pentachlorophenol	ND	ND	ND	ND	ND	6.7	17.2	55.7	58.4	ND

ND = not found or not detectable.

* All data in this table was re-analyzed in June 1983 from sealed capillaries stored in a deep freeze.

† Data were obtained independently by Ada, OK, U. S. Environmental Protection Agency lab GC/MS/DS. Quantitation was based upon an internal standard of D_{10}anthracene at 20 ng/µl and upon relative response factors.

Sep-Pak cartridges used for rapid sample preparation simplified analyses in routine tests. Sep-Pak cartridge sample preparation allowed concentration of low level organic from large volumes of water, could be performed at the sample site, and eliminated the need for liquid-liquid extractions. The advantages of Sep-Pak procedures are: they are more versatile than solvent extractions, more accurate, reliable, time-saving, easy to perform, and less expensive. The reproducibility of triplicate samples by the Sep-Pak procedures from one liter aqueous solution at 20 ppm concentration level are summarized in Table 3. The range of % C.V. is 0.3 to 7.8 for the first eleven compounds and 14.2-21.2 for the last three compounds.

Water soluble fractions of Conroe pit soil were analyzed by the Sep-Pak procedure. The range of % C.V.'s of three soil replicates after GC analyses was 1.7 to 29.6. The major organic compounds in water soluble fractions of Conroe pit soil were pentachlorophenol, 2,6,10,15-tetramethylheptadecane, pentacosane, pentatricotane and docosane.

In the future, the concentrations of inorganic and trace level organic constituents will be monitored using the above procedures to determine the long-term variability at the Conroe hazardous waste site.

Table 3

Recovery and Reproducibility of Triplicate Samples by Sep-Pak Procedures from One Liter Aqueous Solution at 20 ppm Concentration Level

Spiked compound	Concentration determined	Recovery (%)	% C.V.
1,2,3-Trimethylbenzene	15.59 ± 0.89	77.95 ± 4.45	5.7
p-Chlorobenzene	16.11 ± 0.66	80.55 ± 3.3	4.1
Fenchone	20.32 ± 0.38	101.60 ± 1.9	1.9
Borneal	18.92 ± 1.16	94.6 ± 5.8	6.1
Naphthalene	17.80 ± 0.53	89.0 ± 2.65	3.0
2-Methylnaphthalene	17.86 ± 0.27	89.3 ± 1.35	1.5
1-Methylnaphthalene	18.48 ± 0.06	92.4 ± 0.3	0.3
Biphenyl	18.53 ± 0.33	92.65 ± 1.65	1.8
1,7-Dimethylnaphthalene	17.23 ± 0.17	86.15 ± 0.85	1.0
Dibenzofuran	18.49 ± 0.95	92.45 ± 4.75	5.1
Fluorene	19.28 ± 1.50	96.40 ± 7.5	7.8
1-Methylfluorene	18.79 ± 2.67	93.95 ± 18.55	14.2
Dibenzothiophene	19.43 ± 3.7	97.15 ± 18.55	19.1
Anthracene	12.16 ± 2.58	60.8 ± 12.9	21.2

IRREVERSIBLE SORPTION OF TRACE LEVEL ORGANICS BY GROUND WATER HUMIC SUBSTANCES: A NEW MECHANISM OF TRANSPORT

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ABSTRACT

Soil column experiments exhibited mediated transport of hexachlorobenzene (HCB) by a ground water humic material (HM). The retardation equation was modified to include transport of a dissolved HCB/humic complex in the mobile aqueous phase in an attempt to account for the mediated transport. It appears that the mobilized HCB moves conservatively through the column in an apparently irreversible manner.

INTRODUCTION

That neutral, or hydrophobic, organic compounds can bind to sediments and soils through interaction via the humic materials of those sediments and soils has been demonstrated by a number of authors (Karickhoff *et al.*, 1979; Davidson *et al.*, 1980; Lopez-Avila and Hites, 1980). More recently this work has been extended to the dissolved organic, or humic, materials in water (Hassett and Anderson, 1979; Wershaw *et al.*, 1969; Poirrier *et al.*. 1972; Matsuda and Schnitzer, 1973; Carter and Suffet, 1982). It has been suggested that the effect of organic/humic interactions could significantly alter the subsurface fate of organic contaminants. In the research presented here, the transport of HCB through a soil column, in the presence of a humic material isolated from a ground water, was observed. The effect of humic/organic interactions on the fate of organics in the subsurface environment was examined.

EXPERIMENTAL PROCEDURES

Isolation of a Ground Water Humic.

Humic material was concentrated and isolated from a ground water obtained from a control well on an abandoned creosoting site in Conroe, TX. This site is currently being studied by Rice University. Analysis of the water is as follows: TOC = 0.5 mg-1^{-1}; conductivity = 82 μmhos-cm^{-1}; turbidity = 0 FTU's; pH = 4.40 and chlorides = 13 mg-1^{-1}. Approximately 2000 l of ground water was pumped from 25 ft by peristaltic pump (Cole-Parmer, Chicago, IL) equipped with polyethylene and tygon tubing at a rate of 80 1-day^{-1}. Prior to collection, the well was flushed of several well volumes. The humic and fulvic acids were collected from the water by Amberlite XAD-8 adsorption chromatography (Thurman and Malcolm, 1981). The final lyophilized isolate was 294 mg of a light, fluffy, yellow material.

Soil Column.

The column used in this study is a 15 cm × 0.9 cm I.D. borosilicate glass column (Spectrum Scientific, Houston, TX) which had been used to study breakthrough of target organic compounds in the influent of a rapid infiltration site in Ft. Polk, LA (Waggett, Master's Thesis, 1984). The column was packed with soil from the Ft. Polk site. Analysis shows the soil to be 0.2% organic matter (≈ 0.12% organic carbon, Lyman, 1982), 9.9% silt, 26% clay and is classified as a sandy clay loam.

Feed Solutions.

Feed solutions contained either hexachlorobenzene (HCB), humic material (HM) or both and were prepared in ground water obtained from the Ft. Polk site. The total organic carbon content of the ground water, as determined by two adjacent wells, was 1-3 mg-1^{-1}. The ground water was 0.45μ filtered (Millipore Corp., Bedford, MA). Sodium azide was added at a concentration of 5.0 mg-1^{-1} to control microbial growth. Carbon-14 labeled hexachlorobenzene in benzene purchased from Pathfinders (St. Louis, MO) was added by evaporating the benzene from the solution in a volumetric flask, adding the ground water solution and stirring for 24 hrs. Specific activity was 9.14 mCi/mmol and purity 98^{+}%.

EXPERIMENTS AND RESULTS

The following experiments were run in the order listed. Feed solutions were pumped by Spectra-Physics Model 8000 HPLC pump at a flowrate of 0.055 ml-min^{1} (5.7 × 10^{-3} cm-s^{-1}) and were aluminum foil wrapped at all times. Effluent concentrations of HCB were determined by counting one ml aliquots collected directly into scintillation cocktail (Ready-Solv™ HP, Beckman Corp., Houston, TX) by fractionator. Samples were counted by a packard Trias liquid scintillation counter with a preset error of 5% σ.

HCB and HM.

The feed solution was prepared contained 20 μg-1^{-1} C^{14}-HCB and 20 mg-1^{-1} ground water humics (9.0 mg-1^{-1} organic carbon). The solution was equilibrated for 24 h prior to use. Hexachlorobenzene was detected in the column effluent at 1 h (1.4 pore volumes), and at 17 h (23.8 pore volumes) the HCB concentration stabilized at 0.92 μg-1^{-1} (Figure 1). At 112 the feed solution was switched to unspiked ground water.

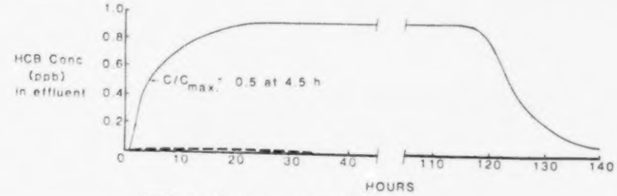


FIGURE 1. Column Breakthrough of HCB-HM Complex

HCB Only.

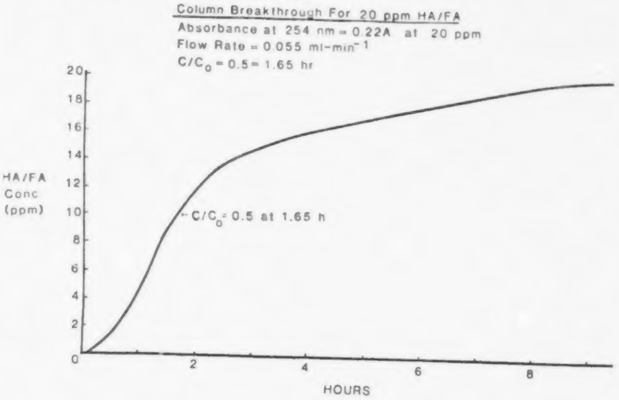
The feed solution contained 20 μg-1^{-1} C^{14}-HCB only. The HCB concentration was monitored as before. HCB was again detected at 1 h, and remained at 0.05 μg-1^{-1} throughout the experiment.

HM Only.

The feed solution contained 20 μg-1^{-1} (9.0 mg-1^{-1} organic carbon) HM isolated from the Conroe ground water. The HM effluent concentration was monitored by UV absorbance of 254 nm in a flowthrough cell. The HM concentration in the effluent was 20 mg-1^{-1} (Co) in 9 h (12.6 pore volumes) and the C/Co = 0.5 occurred at 1.65 h (2.3 pore volumes) (Figure 2).

FIGURE 2

Column Breakthrough For 20 ppm HA/FA



CONCLUSIONS AND DISCUSSION

HCB column transport was enhanced in the presence of dissolved organic matter. The authors completed a mathematical modification of the retardation equation to include transport of HCB by the dissolved humic material in the aqueous phase. Following the derivation approach used by Said (1979):

$$V_{av} = f_1 V_1 + f_2 V_2 \text{ -----} \qquad (1)$$

The average velocity of a group of solute contaminant molecules, V_{av}, is given by this equation. It is assumed that a fraction of the molecules, f_1, has velocity V_1, etc. There are only two fractions of solute molecules in our problem, those which move with the mobile phase (water) which have a velocity V_w, and those which are associated with the stationary phase, f_2, of velocity $V_2 = 0$:

$$\begin{aligned} V_{av} &= f_1 V_1 + f_2 V_2 = f_1 V_1 \qquad (2) \\ &= V_w \text{ (fraction of solute in the water plus the dissolved organic matter (DOM))} \end{aligned}$$

The fraction of solute in the mobile phase, f_1, can be calculated:

$$f_1 = \frac{m_{aq} = m_{om}}{m_{aq} + m_{om} + m_{os}} \qquad (3)$$

where: m_{aq} = solute mass in the aqueous phase
m_{om} = solute mass in the DOM
m_{os} = solute organic mass in the soil organic matter

$$K_p^{om} = \frac{C_{om}}{C_{aq}} \qquad (4)$$

where:

C_{om}, C_{aq} = concentration of solute in the mobile DOM phase and aqueous phase, respectively

$$= \frac{m_{om}/V_{om}}{m_{aq}/V_{aq}} \qquad (5)$$

where:

V_{om}, V_{aq} = volume of the DOM and aqueous phases, respectively

For simplicity, the density of all phases has been assumed to be 1.00 g/ml. Also, we are only looking at the soil organic matter, not the whole soil phase. Similarly:

$$K_p^{os} = \frac{m_{os}/V_{os}}{m_{aq}/V_{aq}} \text{ for the soil organic phase.} \qquad (6)$$

Using equations 5 and 6, f_1 can be solved and substituted into equation 2. If $K_p^{om} = K_p^{os} = K_p$ then the final form of the modified retardation equation is:

$$R = \frac{V_w}{V_c} = 1 + \frac{K_p \frac{V_{os}}{V_{aq}}}{1 + K_p \frac{V_{om}}{V_{aq}}} \qquad (7)$$

Using equation 7 with 20 ppm dissolved organic carbon and 0.02% soil organic carbon would predict 50% breakthrough at greater than 100 hrs. In the experiment one-half the final steady state concentration occurred at 4.5 hrs. Therefore, there must be some additional mechanisms of transport which results in an "irreversible" (or kinetically slow) complex formed between HM and HCB.

In conclusion, it appears that dissolved organic matter can form an irreversibly bound complex with hexachlorobenzene which is mobilized in soil column and represents a new mechanism by which ground waters can be contaminated.

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ORGANIC SOLUTE TRANSPORT IN GROUNDWATER DISCHARGE ENVIRONMENTS

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ABSTRACT

The advective flux of organic pollutants to surface waters from contaminated groundwater was measured using an in situ column technique. These columns are 20-cm diameter, 30-cm long cylinders that are inserted vertically in shallow-water sediments known to be receiving groundwater. A tracer mixture, e.g., tritium and naphthalene, is injected into a screened disc at the column base. A sampling tube near the column top permits tracer monitoring over time.

This study was prompted by the observation that trace organics travel hundreds of meters from municipal waste sites through sandy aquifers to nearby surface waters yet no device existed to monitor this pollutant influx. The in situ column was field tested by determining the sorption behavior of ^{14}C-labelled naphthalene at concentrations less than 0.01% of its water solubility.

Results show that it is practical using in situ columns to determine retardation factors for selected organics in groundwater discharge environments such as stream beds. Preliminary tracer test data show naphthalene retardation about one-fifth that predicted from its n-octanol/water partition coefficient and the organic carbon fraction of the sediments.

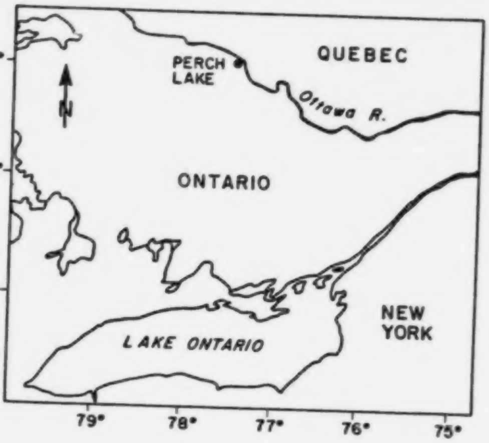

Fig. 1. Location of Perch Lake in Eastern Ontario.

INTRODUCTION

Several recent studies have addressed the problem of predicting trace organic migraiton in aquifers (McCarty et al., 1981) and during infiltration (Roberts et al., 1980; Wilson et al., 1981; Schwartzenbach et al., 1983). However, none has attempted to directly observe the transport of trace organics in groundwaters at their point of entry into surface water bodies.

Our purpose here is to describe an in situ column tracer technique for determining the transport behavior of ^{14}C-labelled trace organic solutes that can be used in sandy groundwater discharge environments such as lakes, streams and estuaries. Our method has the advantage as of using undisturbed sediments and naturally discharging groundwater in chemical equilibrium with its porous medium. Field testing of the device was limited to a hydrophobic trace organic (i.e., a nonpolar and non-ionic organic solute at 10^{-4} to 10^{-2}% of its water solubility) to ensure that the observed organic retardation was due predominantly to hydrophobic sorption, rather than to interactions with the mineral fraction of the sediments. ^{14}C-labelled naphthalene was chosen for the field test of the apparatus because, although some retardation of this compound could be expected (naphthalene has a Log K(ow) of 3.3), it was also likely mobile enough to pass through the column within four to five days. Field retardation factors derived from in situ column tracer experiments using ^{14}C-labelled naphthalene were then compared to a predicted retardation factor based on the n-octanol/water partition coefficient of the compound and the organic carbon fraction of the sediments.

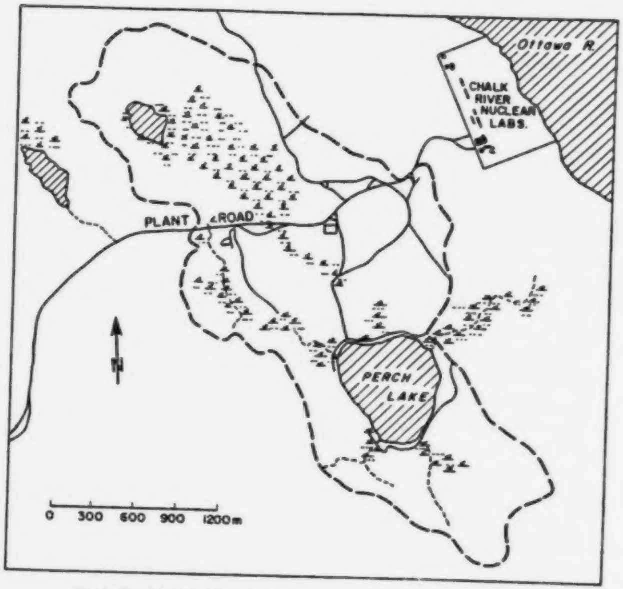

Fig. 2. Perch Lake basin and environs.

STUDY SITE

The field investigation was conducted in a ten by four meter plot of subaqueous sediments in the Perch Lake outlet streambed in eastern Ontario on the property of the Chalk River Nuclear Laboratories of Atomic Energy of Canada Limited (Figures 1 to 3). The general pattern of groundwater discharge is shown in Figure 4.

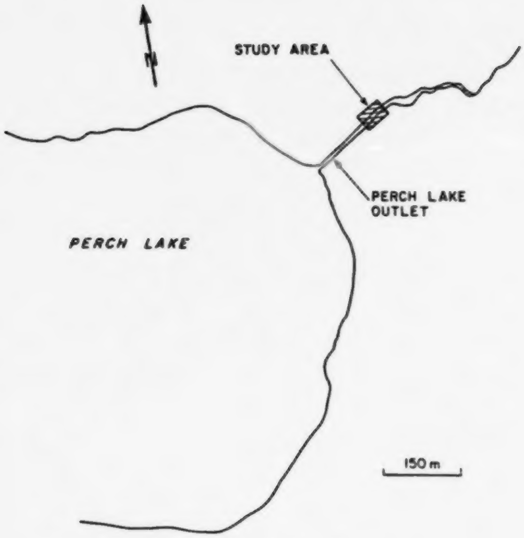

Fig. 3. Location of study area in Perch Lake outlet.

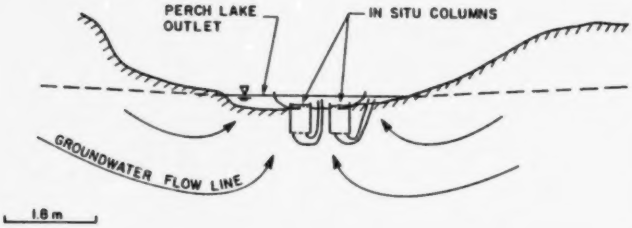

Fig. 4. Schematic diagram of groundwater discharge at the Perch Lake outlet streambed.

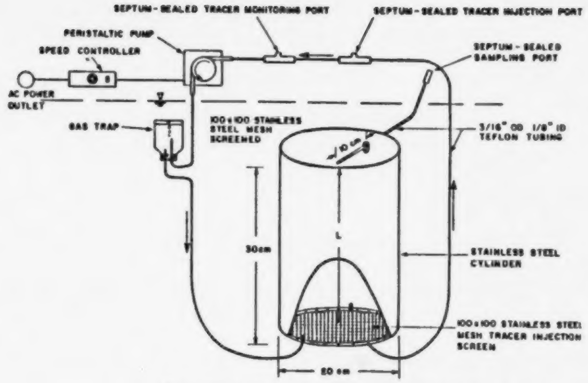
SEPTUM-SEALED TRACER MONITORING PORT
SEPTUM-SEALED TRACER INJECTION PORT
PERISTALTIC PUMP
SPEED CONTROLLER
AC POWER OUTLET
SEPTUM-SEALED SAMPLING PORT
GAS TRAP
100×100 STAINLESS STEEL MESH SCREENED
3/16" OD 1/8" ID TEFLON TUBING
10 cm
L
30cm
STAINLESS STEEL CYLINDER
100×100 STAINLESS STEEL MESH TRACER INJECTION SCREEN
20 cm

Fig. 5. The in situ column plus tracer pulse mixing apparatus.

MATERIALS AND FIELD METHODS

The in situ column is an adaptation of a device used by McLeod (1982) for inorganic solute tracer tests. All parts are made of either PTFE (polytetrafluoroethylene or Teflon® or stainless steel to minimize sorption of organics to the column material. The apparatus (Figure 5) consists of (1) a thin-walled 30-cm long by 20-cm diameter stainless steel cylinder; (2) a small-volume finely-screened PTFE groundwater sampling tube (3/16" O.D., 1/8" I.D.); and (3) a 19.5-cm diameter, one-centimeter thick stainless steel and PTFE porous tracer injection screen with PTFE tracer inflow and outflow tubes (3/16" O.D. 1/8" I.D.). During the tracer pulse mixing period (discussed below), one to two meters of additional PTFE tubing, a variable speed peristalitc pump and a gas trap were also required.

The upper groundwater sampling tube consists of a 15- to 20-cm PTFE tube perforated about five centimeters from one end and covered with a fine stainless steel screen. During column installation the screened tip of the tube is passed through a rubber stopper and inserted in a two centimeter hole about 10 cm from the top of the cylinder. The sampling tip is positioned approximately mid-way across the column diameter (see below on column installation).

The tracer injection screen is designed to introduce a well-mixed tracer pulse at the column base where it is then carried by upward-moving groundwater. The screen consists of two one-centimeter wide PTFE rings, placed above and below two fine-mesh stainless steel screens, and held together with stainless steel bolts (Figure 6). Two coarse screens, inserted between the fine screens, provide space for the circulation of the tracer solution. Opposing tracer inflow and outflow tubes were inserted through holes in the PTFE rings. A flow path for tracer pulse mixing was maintained by two short stainless steel tubes that were inserted into holes in the inflow and outflow tubes (Figure 6). The open ends of the inflow and outflow tubes were sealed with stainless steel bolts.

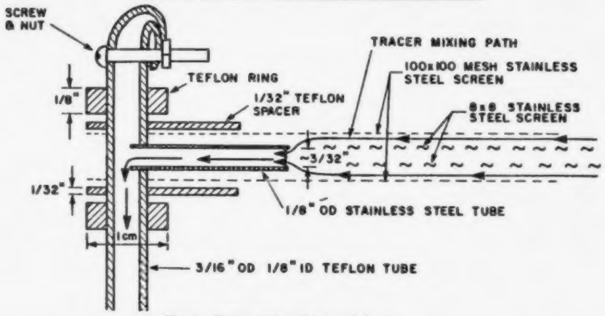
SCREW & NUT
TRACER MIXING PATH
100×100 MESH STAINLESS STEEL SCREEN
TEFLON RING
1/32" TEFLON SPACER
8×8 STAINLESS STEEL SCREEN
1/8"
~3/32"
1/32"
1/8" OD STAINLESS STEEL TUBE
1cm
3/16" OD 1/8" ID TEFLON TUBE

Fig. 6. Cross section of tracer injection screen.

During the tracer pulse mixing period, one to two meters of additional PTFE tubing was attached to the outflow or suction side of the injection screen and coupled in sequence with two stainless steel union tee connectors (Figure 5). PFTE-faced silicone rubber septa, inserted in union tees, provide access by needle and syringe to the tracer flow path for tracer injection and sampling.

Once an appropriate discharge site was chosen, an in situ column was installed by inserting the metal cylinder vertically into the sediments and slowly turning until the top of the cylinder was about five centimeters above the sediment surface but at least 10 cm below the water surface. Four 24-cm long cores were then taken from around the outside of the cylinder with two-inch diameter aluminum pipe (Figure 7). A hole immediately adjacent to the cylinder was then

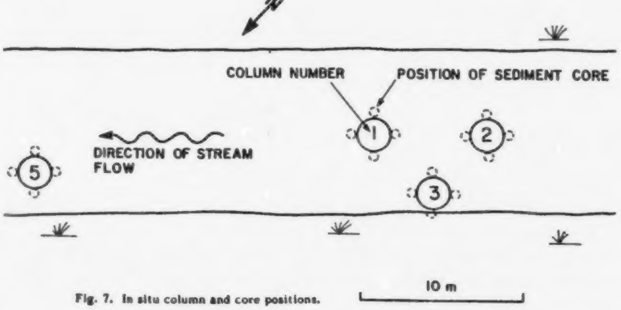

Fig. 7. In situ column and core positions.

excavated. When the base of the cylinder was exposed, the tracer injection screen was pushed horizontally beneath the cylinder. Care was taken to ensure that the cylinder completely surrounded the injection screen and that the inflow and outflow tubes were not crimped by the cylinder or by sediment. Columns were allowed to flush for two to four weeks. During the flushing period and throughout the field season, frequent seepage measurements were made by sealing the column with a rubber-backed plate and collecting seepage through a small hole in the top.

Prior to any organic tracer experiments, the amount of time required for the naphthalene pulse or slug to break through the column was estimated based on the average linear groundwater velocity ($\bar{v}$) of the column, the n-octanol/water partition coefficient (K(ow)) of the naphthalene, and an estimate of the sedimentary organic carbon fraction (F(oc)) or about 0.001 grams of organic matter per gram of sediment. An adaptation of the retardation equation (Freeze and Cherry, 1979) was used:

$$\bar{v}/\bar{v}(c) = 1 + K(p) \times b/n \tag{1}$$

where $\bar{v}$ (c) is the velocity of the center of mass of a contaminant, (K(p) is the solute/sediment partition coefficient, b is the bulk density of the sediment (assumed constant at 1.58 grams/cm^3) and n is the porosity of the sediment (assumed constant at 0.38) (McLeod, 1982). From Karickhoff and others (1979) we further assumed:

$$K(oc) = K(p)/F(oc) \tag{2}$$

and

$$\mathrm{Log}(K(oc)) = 1.00 \times \mathrm{Log}(K(ow)) - 0.21 \tag{3}$$

where K(oc) is the solute/sediment organic carbon partition coefficient.

By combining equations (1) and (2) and solving for the time (in days), T(bt), required for an organic breakthrough to occur, we obtained

$$T(bt) = L \times (1 + K(oc) \times F(oc) \times b/n)/\bar{v} \tag{4}$$

where L is the distance from the injection screen to the upper sampling tube. The results of these preliminary calculations are presented on Table 1.

TABLE 1. NAPHTHALENE SORPTION PROPERTIES AND PREDICTED VERSUS FIELD ORGANIC PEAK ARRIVAL TIMES

Water Solubility (mg/L)[a]	Log(K(ow))[a]	Log(K(oc))[b]	Arrival Times[c] Pred. T(bt)[d]	Fld. T(bt)
31.7	3.31	3.10	4.44	0.45 (83/9/30) 0.53 (83/10/16)

[a] Kenaga and Goring, 1980; [b] Log(K(oc)) = 1.00 Log (K(ow)) - 0.21, (Karickhoff et al., 1979); [c] F(oc) = 0.001, b = 1.58 g/cm^3, n = 0.38; [d] $\bar{v}$ = 1.21 cm/hr, L = 21 cm.

Naphthalene-ring-UL-^{14}C- (specific activity 6.12 mCi/mmol, 98% purity) was obtained commercially from Pathfinder Laboratories (St. Louis, Missouri). Tritium in the form of tritiated water was obtained from the radioisotope laboratory of the Environmental Research Branch at the Chalk River Nuclear Laboratories, Chalk River, Ontario.

For about 30 to 60 minutes prior to the injection of the tracers, the water within the injection screen and associated tubing was circulated in a closed loop at 50 to 100 mL per minute to ensure the complete mixing of groundwater through the injection screen and past the injection port. At the desired injection time, a 50-mL glass syringe with a known amount of concentrated aqueous ^{14}C-naphthalene and tritium was brought to the field. With the groundwater circulation pump on, the syringe contents were slowly injected (i.e., over a duration of two to three minutes) into the suction side of the circulation loop. After two hours of tracer pulse circulation the pump was turned off.

All groundwater tracer samples were obtained at the upper sampling port which consists of a PTFE-lined silicone rubber septum inserted in a stainless steel reducing union (Figure 5). Immediately before and after the two-hour tracer pulse mixing period, a 25-mL groundwater sample was taken from the upper sampling port with a 50-mL glass syringe. Subsequent groundwater samples were taken in this manner every one to six hours until background activity within the column was restored. Groundwater tracer samples were stored with no head space in the dark in organic-free 25-mL scintillation vials at 4°C until analyzed.

Samples were analyzed by liquid scintillation counting for both ^{14}C and tritium on a Beckman LS-230 liquid scintillation counter within six to eight hours of withdrawal from the field. Of the 25-mL sample, a one-milliliter aliquot was counted with ten milliliters of scintillator (Scintiverse I Universal Scintillation Cocktail, Fisher Chemical). Samples were counted for at least five counting cycles, with each cycle having a duration of ten minutes. ^{14}C and tritium sample counts were corrected for background activity.

RESULTS

In situ column and core positions (including three columns not discussed in this paper) are illustrated in Figure 7. Average linear groundwater velocities ($\bar{v}$) of column 1 were calculated assuming a sediment porosity of 0.38 and are presented in Table 2. The results of sedimentary organic carbon and grain-size analysis on sediment cores are presented in Table 3. According to the inclusive graphic standard deviation (sigma I) described by Folk (1980), the sands from cores near column 1 were well- to moderately well-sorted. Concentrations of organic carbon in the sediments (F(oc))ranged from 0.00064 to 0.00190.

TABLE 2. SELECTED COLUMN SEEPAGE RATES

Date	Average Linear Groundwater Velocity ($\bar{v}$), cm/hr[a]	
83/9/18	1.35	
83/9/25	1.28	
83/12/22	1.07	
83/12/22	1.20	Mean $\bar{v} \pm \sigma = 1.21 \pm 0.09$
83/12/22	1.27	
84/1/4	1.20	(n = 8)
84/1/5	1.17	
84/1/5	1.16	

[a] Values calculated by $\bar{v} = Q/An$, where Q = volume seepage collected (L^3), A = cross-sectional area of the column (L^2), n = assumed sediment porosity of 0.38.

TABLE 3. SEDIMENT CHARACTERISTICS

Column 1 Core Position,[a] Date	Mean Grain Size, mm	Sigma I[b]	F(oc)[c]
SW, 83/7/12	0.180	0.5 ϕ	0.0019
NE, 83/7/12	0.120	0.6 ϕ	0.00064

[a] SW = southwest core, NE = northwest core; [b] Sigma I represents the spread of phi (ϕ) units of a sample. Values 0.35 ϕ to 0.50 ϕ well-sorted. Values 0.50 ϕ to 0.71 ϕ are moderately well-sorted (Folk, 1980). [c] Analysis was by $CO_2(g)$ trapping of combusted sediments using a Leco induction furnace coupled to a Beckman infrared analyzer.

On 83/9/30 a simultaneous tritium and ^{14}C-naphthalene tracer experiment was conducted with column 1. The resulting breakthrough curves are presented in Figure 8. Additional data are presented in Ta-

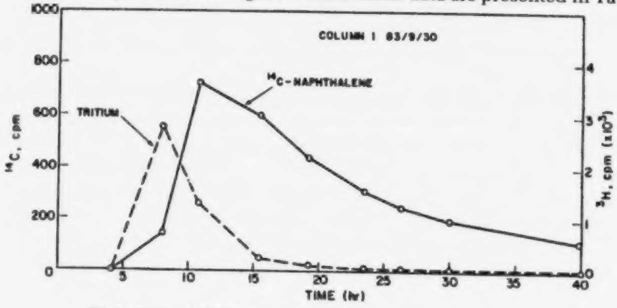

Fig. 8. Column 1 83/9/30 tritium and ^{14}C-naphthalene breakthrough curves.

ble 4. Although sampling intervals were too long to delineate clearly all inflections points on the breakthrough curves, the position of the naphthalene concentration maximum or peak to that for tritium reveals a small but measurable amount of retardation for naphthalene (Figure 8). A retardation factor was calculated by dividing the observed arrival time of the naphthalene concentration peak by the observed arrival time of the tritium concentration peak. By this method, the naphthalene retardation factor for the 83/9/30 experiment was found to be 1.37 (Table 4).

TABLE 4. TRACER TEST DATA

Experiment date	83/9/30	83/10/16
Mean column flow velocity ($\bar{v}$), cm/hr.	1.21	1.21
Approximate distance of injection screen to sampling point (L), cm.	21	21
Estimated concentration of naphthalene within injection screen at t=0, mg/L.	5.46×10^{-2}	3.19×10^{-2}
Item (4) as per cent of naphthalene's water solubility (WS).	1.72×10^{-1} % WS	1.01×10^{-1} % WS
Estimated concentration of naphthalene at peak concentration, mg/L.	3.00×10^{-3}	5.10×10^{-3}
Item (6) as per cent of naphthalene's WS.	9.45×10^{-3} % WS	1.61×10^{-2} % WS
Predicted naphthalene retardation factor ($=1 + 4.16 \times 10^{-3}$ K(oc)).	6.23	6.23
Field naphthalene retardation factor (based on peak concentrations).	1.37	1.35

The tritium and ^{14}C-naphthalene experiment was repeated on 83/10/16. The resulting breakthrough curves are presented in figure 9. In this experiment a shortened sampling interval of 60 to 90 minutes made it possible to plot most of the inflection points on both the naphthalene and tritium curves. The mobility of naphthalene was similar to that of the preceeding experiment, with a retardation factor of 1.35.

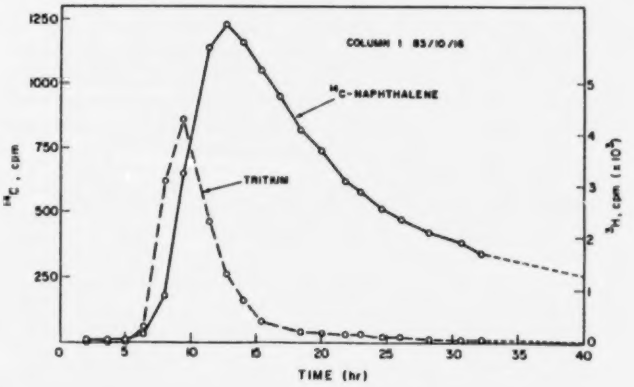

Fig. 9. Column I 83/10/16 tritium and ^{14}C-naphthalene breakthrough curves.

CONCLUSIONS

Two ^{14}C-naphthalene and tritium tracer experiments have shown that an in situ column technique can be applied to a sandy groundwater discharge environment to determine organic solute retardation factors. The average field retardation factor of the naphthalene tracer experiments was 1.36. The predicted retardation factor of these experiments, based on a Log(K(oc)) of 3.10 (Table 1) and a F(oc) of 0.0010 was calculated to be 6.23 (Table 4). Thus, the in situ retardation factor for naphthalene is about 1/4 to 1/5 the predicted value.

The enhanced mobility of naphthalene within the in situ column may have been due to two factors. First, sorption may not have been instantaneous and thus, even at a column groundwater velocity ($\bar{v}$) of about 2 cm/hr we may have seen the effects of slow sorption kinetics which would tend to minimize retardation. Second, although the F(oc) for the column sediment was about 0.001 overall, most of the organic carbon may have been in particles too large to be effective sorbents. Schwarzenbach and Westall (1981) have shown in laboratory column studies that over 85% of hydrophobic sorption takes place on particles less than 0.125 mm. Although more than two analyses are needed to quantify the degree of variability of F(oc) values amongst core samples, the F(oc) values from the sediment cores analyzed so far seem low, i.e., at or less than 0.001, for the grain size range represented, 0.120 to 0.180 mm. Thus, it is possible that the enhanced mobility of naphthalene was due, in part, to a lack of effective organic carbon sorbents in the less-than-0.125 mm particle size fraction, despite the higher over-all F(oc).

On-going sedimentary organic carbon analysis of sediment cores and analysis of data from subsequent column tracer experiments with naphthalene and other ^{14}C-labelled solutes hopefully will shed light on the processes responsible for the observed enhanced mobility of naphthalene.

ACKNOWLEDGEMENTS

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NON-BIOLOGICAL TRANSFORMATION PROCESSES

CHEMICAL TRANSFORMATIONS IN GROUNDWATER

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INTRODUCTION

The presence of chemicals in groundwater is of concern because groundwater is the major source of drinking water for 70% of the US population. Unlike chemicals in surface waters that often are effectively removed via natural or treatment processes and are readily sampled to monitor concentrations, chemicals in the unsaturated region and in groundwater will be a source of chemicals for many years because they move slowly and are not accessible for economical short term remedies. Therefore, understanding how fast the chemicals move in groundwater and the transformation reactions that may alleviate- or create-problems posed by the chemicals is important for future planning of groundwater use. The ability to predict the rates of various transformation processes in groundwater will assist in explaining the persistence or absence of chemicals in these systems, and in guiding future studies as to which properties should be measured and which chemical species (especially products) should be sought in future studies. In this paper we review the chemical transformation processes that may be important for transforming some anthropogenic chemicals in groundwater.

KINETICS OF REACTING SYSTEMS

Evaluation of the important processes that transform chemicals in groundwater systems requires knowledge of the chemistry and the kinetics of the individual reaction processes that may occur in groundwater. For most reactions, the rate of transformation of chemical, C, can be simply represented as a second-order process

$$-dC/dt = k_E[E]\,[C] \qquad (1)$$

where k_E is the second order rate constant for reaction of chemical with an environmental reactant variable E; [E] is the* concentration of an reactant (a reducing agent, hydrogen ion, or even a population of degrading organisms). If [E] is considered constant in some space or time frame (i.e., a regional average value or by a steady state assumption), the half-life for the transformation process is

$$t_{1/2} = \ln 2/k_E[E] \qquad (2)$$

In groundwaters, as in other environments, a number of competing processes may transform a chemical. These processes include hydrolysis, reduction, and oxidation. If the concentration of chemical is low enough so that reaction does not change [E], the rate of transformation of chemical is

$$-dC/dt = k_r[C] = k_{Ei}[E_i]\,[C] \qquad (3)$$

where k_r is the observed first order rate constant for loss of C, and k_{Ei} and E_i are the second order rate constant and concentration terms for the ith process. Equation 3 clearly shows that understanding- and predicting- the rate of transformation of a chemical in a groundwater requires knowledge of both the fundamental reaction rate constant and the concentration of the environmental reactant, [E].

The above approach to evaluating the kinetics of transformation processes is not unique to groundwater environments, and has been usefully applied to surface water systems (Dickson et al. (1982). This approach is straightforward and scientifically sound, and often provides guidance for subsequent studies to better characterize an environment or to consider new processes that bring better agreement between prediction and observation. The approach also has the value that if k_E and [E] are reliably known for one process, a minimum value of k_r can be predicted that may explain the absence of a chemical or allow a decision that the presence of a chemical in a groundwater poses no long term threat to health (i.e., a hydrolysis half-life of 2 years for a chemical that resides in groundwater for 50-100 years will ensure removal of the chemical regardless of whether biotransformations occur).

GROUNDWATER AS A REACTION SYSTEM

The transformation processes that are important for a chemical in a ground water system depend on both the reactivity of a chemical and the identity and concentrations of E in equation 3. Because the routes of chemicals through various environments to groundwater often afford opportunities for hydrolysis, oxidation, and aerobic biodegradation, most chemicals which reach groundwater probably do not react rapidly by these processes. These processes may still be important in groundwater, however, where residence times are very long and other processes are also very slow. Anaerobic groundwaters also provide the possibility of reduction of chemicals via biological or chemical processes.

In evaluating the possible reactions in ground water, one must always recognize that biological, chemical, and physical processes all may determine the properties of and species present in groundwater; reactions of anthropogenic chemicals in these systems will occur regardless of the origin of the reactant variable species. Thus oxidative biotransformations will develop an anaerobic system; this system may also produce sulfide and reduced metal species that may induce purely chemical reactions (see below) that compete with reductive biotransformations.

Groundwaters vary in their character and composition, and to evaluate the possible importance of various types of transformation reactions one must first consider what environmental reactants are present. We then can apply this information to predicting which reactions may occur and possibly explain reaction products found.

Most analyses of groundwater have focused on species related to groundwater quality or to total elemental composition. Except for pH values that are important for hydrolysis reactions, this information generally is not useful for predicting reactions that will occur in groundwater. Other measurements, such as for E_h (potential vs H_2 electrode), DOC, DO, or the presence of sulfate or sulfide, are useful only for describing the groundwater systems in a qualitive way and for inferring the possible presence of some oxidized or reduced forms of the elements present. This lack of information on reactants is due in part to analytical problems or the instability of the reactant species themselves; nevertheless, this information is necessary for understanding the reactions that may occur in groundwater.

In the absence of analytical data on the reactants present in groundwater, the possible species that are most stable may be predicted using thermodynamic arguments. Table 1 lists the half-cell reactions and reduction potentials for the forms of some elements found in groundwaters. The reduction-oxidation (redox) reactions that can occur in groundwater systems are practically bounded by oxidation of water to oxygen as the most oxidizing system, and reduction of protons to hydrogen as the most reducing system. Such a list of redox reactions is a useful beginning to assess the species that may be present under different conditions. Thus the presence of sulfide in a groundwater

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*We use the term reactant variable because modeling loss rates usually involves selecting values of E appropriate for the environment of interest, which may differ widely, whereas the fundamental rate constant is unchanged (except where temperature changes).

Table 1

HALF-CELL REACTIONS AND REDUCTION POTENTIALS[a]

$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$	+ 1.23
$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O$	+ 1.21
$Br_2 + 2e \longrightarrow 2Br^-$	+ 1.09
$Fe^{+++} + e \longrightarrow Fe^{++}$	+ 0.770
$C_6H_4O_2 + H^+ 2e \longrightarrow C_6H_4(OH)_2$	+ 0.699
$O_2 + 2H^+ + 2e \longrightarrow H_2O_2$	+ 0.682
$Cu^{++} + e \longrightarrow Cu^+$	+ 0.158
$S + 2H^+ + 2e \longrightarrow H_2S$	+ 0.14
$2H^+ + 2e \longrightarrow H_2$	0.00

From CRC Handbook of Chemistry and Physics, and Stumm and Morgan (1982).

may indicate that the system is anaerobic and that metals such as Fe or Mn are in a reduced state; therefore, some anthropogenic organics such as alkyl halides may be reduced by these metals.

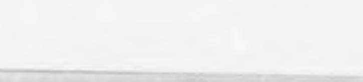
A more complete inventory of the species found in groundwater is provided using a $p\epsilon$-pH diagram that includes the effect of pH and redox potential on the elemental forms present. These diagrams are constructed from thermodynamic data and estimates of the concentrations and species that are of interest. For a given system of species, $p\epsilon$ can be related to E_h (Stumm and Morgan, 1982). Thus, for a measured pH and calculated E_h, we can predict whether nitrogen will be present as NO_3^-, NO_2^-, NH_4^-, or NH_3^+. Similarly, the sulfur species present can be predicted as being SO_4^{2-}, S^o, HS^-, or S^{2-}. Inclusion of Fe speciation in the sulfur system will of course provide a different diagram that includes FeS.

Stumm and Morgan (1982) have emphasized that this thermodynamic approach assumes that the system is at equilibrium, and that in fact many of the reactions are very slow. They note that in surface waters the approach to equilibrium are largely biologically mediated. However, in groundwaters biological activity is probably lower and therefore the approach to equilibrium is much slower than in surface waters; the species present in groundwaters may then be determined by biological and chemical processes, with the latter including both chemical redox reactions and precipitation/dissolution kinetics.

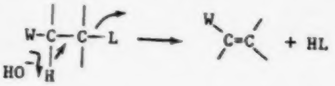
Reactions that may be important in groundwaters may involve species which are intermediates as the system approaches equilibrium. For example, the reduction of sulfate to sulfur must pass through various sulfur oxide species, and further reduction to sulfide may occur via sulfane intermediates. Also, a likely intermediate in the oxidation of Br^- to BrO_3^- is hypobromite, HOBr, which while not thermodynamically favored in a simple $Br^-/BrO_3^-/HOBr$ $p\epsilon$ – pH diagram, may produce brominated products if sufficient concentrations of hypobromite are generated in the presence of reactive organics (see below).

HYDROLYSIS AND pH EFFECTS

Hydrolysis refers to a reaction of a chemical with water, usually resulting in the introduction of a hydroxyl function into a molecule and loss of a leaving group, L. Some of these hydrolysis reactions are catalyzed by specific acid (H_3O^+) or specific base (HO^-) processes and therefore the hydrolysis rates of these chemicals in groundwaters can be pH dependent. Some chemicals also can undergo elimination reactions if the β – carbon (adjacent to the carbon bearing L) has a strong electron-withdrawing group (w) that makes the hydrogen acidic enough for hydroxide ion or water to act as a base.



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-L + H_2O \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH + HL$$



The first order hydrolysis rate constant, k_h, for a chemical at any pH is given by equation

$$k_h = k_A[H^+] + k_B[HO^-] + k_N$$

where $[H^+]$ = – antilog pH, k_N is the rate constant for the pH-independent (neutral) process, and k_A and k_B are the second-order rate constants for the specific acid (H^+) and specific base (HO^-) – promoted processes (Mabey and Mill, 1978).

Hydrolysis may be an important transformation process for a number of halogenated alkanes found in groundwaters. The hydrolysis rates of monohalogenated alkanes are pH independent in the region 3 to pH 11, but some polyhalogenated alkanes show a base-promoted process above pHs 6-7. Table 2 gives the values of k_N and k_B for some chlorinated alkanes along with the hydrolysis half-lives calculated for pH 6 and 25°C (Mabey et al., 1983). Also listed are the pH values at which the rates of the base-promoted and neutral hydrolysis are equal, which we call I_{NB} (intercept where $k_B[HO^-] = k_N$).

The data in Table 2 show that the half-lives and the relative importance of the base-promoted and neutral processes vary with the structure of the alkyl halide and the pH of the water. Also, vinylic chlorides are the products of a base-promoted elimination process for the chlorinated ethanes with $I_{NB} < 8$; trichloroethylene also may be a product from the neutral hydrolysis process of 1,1,2,2-tetrachloroethane. Because the chlorohydrin resulting from the substitution reaction is more readily degraded and probably less toxic than the vinylic halide elimination product, knowing both the kinetics and products of hydrolysis processes is important for decisions on groundwater use (and also for knowing what treatment is required).

Table 2

SUMMARY OF CHLOROALKANE HYDROLYSIS DATA, 25°C

Chemical	$k_N \times 10^{10}$ (s^{-1})	$k_B \times 10^3$ M^{-1} s^{-1}	I_{NB}[c]	$t_{1/2}$ at pH 6
1,2-Dichloroethane	4	0.0013	10.5	50 yr
1,1,2-Trichloroethane	1.2	3.6	6.5	140 yr
1,1,1,2-Tetrachloroethane	0.6	0.36	7.2	350 yr
1,1,2,2-Tetrachloroethane	(2-6) x 10^3	730	7.7	15-40d
1,1,1-Trichloroethane[a]	300	--	> 11	267d
Chloroethane[b]	2100	--	> 11	38d
Chloromethane[b]	237	0.006	11.6	0.9 yr
Dichloromethane[b]	.31	2 x 10^{-5}	11.1	7 centuries
Trichloromethane[b]	.008	0.6	--	> 100 centuries

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[a] Mabey et al., 1983.
[b] Mabey and Mill, 1978.
[c] I_{NB} is the pH at which the neutral and base-promoted processes contribute equally to k_h.

Hydrolysis data for bromoalkanes are less complete, but they do indicate that hydrolytic elimination processes are important for the polyhalogenated alkanes. Thus, Burlinson et al. (1982) reported that the base-promoted elimination process occurs for

1,2-dibromo-3-chloropropane (DBCP) at pHs as low as 7; no data are available to determine I_{NB} for DBCP or whether the neutral hydrolysis products result from substitution or elimination. However, Vogel and Reinhard (1984) have found evidence that elimination is important in both the neutral and base-promoted hydrolyses of 1,2-dibromopropane and possibly 1,2-dibromoethane (EDB). Obviously, more complete kinetic and product studies are required.

OTHER SUBSTITUTION AND ELIMINATION REACTIONS

The hydrolysis reactions discussed above are one class of reactions that are readily studied and applied to predicting the fate of chemicals in aquatic systems, including groundwaters. However, groundwaters also contain other chemical species that are capable of affecting similar substitution and elimination reactions. Thus, the presence of sulfide (as HS^-), carbonate (as HCO_3^-), and other species may contribute to the overall loss rate constant, k_o, of a chemical in groundwater

$$k_o = k_A[H^+] + k_B[HO^-] + k_N + k_R[R]$$

where k_R is the second order rate constant for the reaction of HS^- or HCO_3^- with chemical and [R] is the concentration of the reactant. Such reactions in which species other than H^+ or HO^- act as acids or bases/nucleophiles are referred to as general acid or base catalyzed processes, in which the same ultimate hydrolysis products are often found.

Schwartzenbach et al. (1983) reported that alkyl sulfides were found in a Swiss groundwater, and suggested that reaction between alkyl bromides and HS^- explained their findings. Although more kinetic studies must be performed, this explanation is reasonable if we consider the relative nucleophilicities of HS^-, HO^-, and water. Swain and Scott (1953) have developed a set of constants that express the relative nucleophilicities of various ions (Table 3) in substitution (i.e., displacement) reactions. These data indicate that HS^- is a better nucleophile than HO^- or water; thus, under highly anaerobic conditions at moderate pHs where HS^- may be present at high concentrations, reaction of an alkyl bromide with HS^- may be the dominant reaction process.

Table 3

NUCLEOPHILICITY CONSTANTS[a]

Ion	n[b]
$S_2O_3^=$	6.4
$SO_3^=$	5.1
SH^-	5.1
I^-	5.0
HO^-	4.2
Br^-	3.9
$HPO_4^=$	3.8
HCO_3^-	3.8
$SO_4^=$	2.5
H_2O	0.0

[a] Swain and Scott, 1953.

[b] n is defined by the equation $\log(k/k_o) = sn$ where k and k_o are the rate constants for reaction with an anion and water respectively, and s is a factor for the susceptibility of a reaction to nucleophilic attack (s = 1 for CH_3Br in water solvent).

The data in Table 3 also show that nucleophilic reactions with reactants such as HCO_3^-, $HPO_4^=$, and other species present in groundwater may be important if their concentrations are high enough. If we assume that the nucleophilicity of ions roughly parallels their basicity, we also may expect that HCO_3^- or HS^- may also catalyze the elimination process for the polyhalogenated alkanes discussed above. These reactions require further study, and may be important for accurately predicting the products and loss rates of halogenated alkanes in groundwaters.

REDUCTION REACTIONS

Anaerobic groundwaters are systems that may provide species capable of chemical reduction of certain classes of anthropogenic chemicals. As noted above, the presence of an anaerobic system and various reducing agents may arise from both biological and chemical processes. Most of the reduction reactions of organic chemicals studied have been related to reactions involving reduced metal ion species in biological systems. Thus, Castro et al. (1983), have reported reduction of chloropicrin by microorganisms; subsequent studies found that an enzyme system isolated from the organisms and iron porphyrin also reduced tetrahalogenated methanes to chlorform (Castro, 1984). EDB also has been reported to be reduced to ethylene by biological systems (Castro, 1968). Other work has discussed the reduction of DDT by metal-ions in biological systems (Stotter, 1977).

There are examples of reduction of organic halides in purely chemical systems, however. Williams and Bidleman (1978) found that toxaphene was reduced to less chlorinated products by a Fe^{2+}/Fe^{3+} system. Glass (1973) reported that DDT was reduced by Fe^{2+}. Thus, Fe^{2+} in anaerobic systems may reduce organic halides. However, there are no kinetic data to estimate the rates of these reactions, and the speciation of Fe^{2+} (probably as sulfide and hydroxides) must be evaluated before any kinetic work is conducted.

OXIDATION REACTIONS

There are no kinetic data with which to evaluate the importance of chemical oxidation processes in groundwater systems. Any studies of groundwater chemistry must, of course, recognize the possible importance of biological processes. However, the finding of oxidizing species such as Cr^{6+} do offer the possibility that chemical oxidation processes are important under appropriate conditions (Robertson, 1975). A more complete analysis and description of the oxidants present in groundwaters must be developed before chemical oxidation studies are conducted.

One example of a chemical oxidation process that may occur in groundwater may explain the presence of bromoform in some groundwaters; bromoform has been found in a water emanating from groundwater source in California that has no obvious source of anthropogenic alkyl halides (Fretwell, 1984). Thus, under oxidizing conditions and in the presence of high concentrations of Br^-, Br^- may be oxidized to BrO_3^-. This oxidation may proceed via hypobromite, which is known to brominate fulvic acid to produce bromoform in a reaction analogous to the production of chloroform in the chlorination of humic substances (Malcolm, 1984). Obviously, some careful kinetic and product studies are necessary to support or refute this mechanism for bromoform formation.

CONCLUSIONS

The above discussions of the chemical transformation processes that are or can be in ground water range from reliable data (such as for hydrolysis) to speculation (as for oxidation). Clearly, groundwater systems must be better characterized in terms of the important species that are present in different types of groundwaters. This work will require the collaboration of those that analyze the groundwaters (for both the anthropogenic and natural species present,) and those with expertise in evaluating the kinetics of the reactions. Part of these studies must include kinetic studies on the rates of dissolution and redox reactions of the "natural" species present to determine the relative importance of the biologically mediated and purely chemical processes.

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GEOCHEMICAL INVESTIGATIONS INTO GROUNDWATER POTENTIAL CONTAMINANTS RESULTING FROM UNDERGROUND COAL GASIFICATION (UCG)

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ABSTRACT

UCG is a process by which subbituminous coal is pyrolyzed in situ and the product gas is recovered above the ground. The process involves thermal decomposition of coal and other rock material immediately surrounding the coal stratum. Ash, tar, charcoal and pyrometamorphic materials are produced, and inorganic minerals along with organic gases are liberated and released into the surrounding coals, which are fractured, saturated and form a component of the groundwater system. The vaporized organic gases condense to form pollutants including phenols and pyrines, which are subsequently absorbed by the reactive surfaces of the decomposed coal products. Aromatics, such as benzene and toluene, move faster in groundwater than the heavier molecular weight organics. Both parameters show erratic distribution in post-burn groundwater samples. Phenols were not found in high concentrations, with the process wells portraying the lowest concentrations. Several years after test gasifications were terminated, most of the parameters, excluding sulfate, have returned to pre-test levels. If the high sulfate condition can be dealt with, long term detrimental effects can be discounted.

At the time of writing, U.S. work has been confined to limited scale field tests. Possible water quality effects appear to be the result of test procedures, i.e. premature shut-down, and would be absent under production conditions.

Groundwater contamination from UCG operations is site specific and depends on original coal chemistry, overburden rock composition, aquifer characteristics, and hydrologic and geologic controls. Chemical studies showed high post-test concentrations of sulfate, ammonia, conductivity, barium, total organic carbon, chemical oxygen demand, calcium, and organics. All these parameters, except sulfate, decrease to pre-test levels with time.

Most of the groundwater organic and inorganic contaminants were leached from the decomposed coal products by CO_2-charged groundwater and change in redox conditions. Groundwater composition evolves as a result of the reaction between the UCG generated gases and the original or thermally induced mineralogical changes. Mineral saturation indices calculated from chemical data indicate that cavity waters from the three gasified sites display difference in calcite and gypsum stability conditions. Gypsum is under-saturated and would probably dissolve, while calcite is over-saturated. Trends in calculated COD/TOC ratios are useful in predicting changes in oxidative capacity with time and map changes in the distributional patterns of redox environmental conditions in hydrochemical systems.

INTRODUCTION

Changes in groundwater chemical composition and, in some cases, local intercommunication between aquifers is of concern in areas adjacent to shut-down Underground Coal Gasification test sites. In certain cases, where water flows through the coals through the burn sites, there is evidence that the system is self-restoring, at least for organic by-products.

This paper addresses observed water quality changes and examines cause and effect from a geochemical viewpoint.

The entire suite of phenomena appear to be an artifact of the limited-scale test work and pilot scale activities which lead to premature shut-down involving uncompleted combustions. In production conditions, volatiles driven outward by burn zone operating pressures are adsorbed on the surrounding virgin coals, later to be burned by the advancing combustion zone. The net inflow of water necessary for efficient gas production means that water resources, rather than water quality, are more likely to be the concern of long term production operations.

During underground coal gasification, volatile organics which do not report in the production gas stream are driven by high reaction pressures to migrate through fractures out into the coal formation. The velocity with which these volatiles move and the distance they travel through the formation is a function of the reactivity of the adsorping media, parameters to be exchanged or adsorped, type of organics/clays, the permeability of the surrounding coals, and the hydraulic patterns resulting from process water requirements.

Chemical evolution of local groundwater, resulting from UCG test operations, involves the interaction of highly reactive residual coal and thermally altered minerals with activated groundwater. To predict establishment of long-term thermodynamic equilibrium conditions requires a study of the types and effects of induced mineralogical changes and hydrogeochemical systems on the composition of groundwater.

Groundwater analyses is by nature stochastic. One of the greatest concerns in groundwater evaluation is the uncertainties in analytical data and variations in sampling procedures. Errors from different sources that are introduced, include (1) improper sampling techniques; (2) inadequate sample preservation procedures; (3) sample contamination, (4) sampling inconsistencies.

Ground Water Sampling, Inc. has pioneered the application of sampling theory and the development of efficient sampling installations for subsurface water quality monitoring.

Uncertainties of original water composition originating in unsatisfactory sampling methods can be resolved if proper statistical methods are performed on pre-test analytical results. Geostatistical analyses in conjunction with sound hydrological and geochemical interpretations will explain the spatial and temporal changes in groundwater quality. Geostatistics differ from classical statistics in the sense that in the former, the attributes of a sample are related to regional scale and that the data points are not assumed to be independent of each other. For example, the content of sulfate in groundwater at one location is definitely related to the concentration in a nearby sample.

Gasification characteristics of various sites can be different, depending primarily on permitted water inflow, operating temperatures and pressures. The reaction site or chamber may operate as a true gasification or as a pyrolysis or coking reactor. Pyrolysis involves thermal decomposition of coal when a seam is subjected to temperatures above 700°F (approx. 400°C). This reaction produces gases and tar. Minimum kinetics are required in breaking bonds and the resulting reactions, which are controlled by temperature and heating value, are irreversible. Coal gasification, on the other hand, depends on reaction kinetics where in the reactor chemical reaction predominates as char and other combustible gases are consumed, producing in the process, combustible gases which do not evolve during coal pyrolysis. Methane production is favored under the low temperature and high water influx rate and steam (source of hydrogen) conditions encountered at pyrolysis-type turns. At 1100°F (approx. 600°C), gases approach equilibrium for both gasification and methenation reactions. The great amount of steam generated at one site probably altered the composition of the volatile gases and the resulting char.

The objectives of this study are:

1) To identify organic and inorganic elevated species in groundwater (SO_4, HCO_3, TOC, DOC, Fe, and Phenols) and suggest possible causes for the observed changes and trends in post-test groundwater.
2) To elucidate, utilizing thermodynamic equilibrium activity calculations, groundwater chemical systems in terms of stability relationships between mineral phases present in the modified composition of groundwater.

3) To calculate reducing conditions (pE) of the present coal formation groundwater from redox conditions of the HS-SO_4 system and observed trends and possible causes of sulfate reduction.

GEOLOGY AND ENVIRONMENTAL FACTORS

Historically, UCG sites were selected from economically unattractive sections of the vast western coal resources, and range from deep thick coals to thin coals in steep digging formations. Successful development of UCG methods may provide alternative energy supplies to supplement current conventional systems. Environmental impacts would be comparable in magnitude with that of heavy oil recovery using the combustion method.

Under full scale operating conditions a net inflow of water occurs, water being necessary to the process. Thus, water consumption is the primary concern.

However, when test sites are closed on partially burned coals and natural flooding occurs, infiltration of pyrolysis products becomes a concern.

Coal deposits are commonly underlain by impervious beds and, at least at the time of deposition, overlain by plastic clay-shale aquicludes. The heat of combustion encourages overlying formation collapse, and communication is established between the fracture-permeable coals and overlying aquifers. Water interchange occurs, and flows through the reaction zones.

GEOLOGY

The coal seams are overlain by locally indurated calcareous sandstones, interbedded with clayey lignitic units, which in turn, is overlain by carbonaceous clayey siltstones and associated sandstones. These clayey units, which contain secondary nodules of siderite, easily wash out during drilling.

AQUIFERS

Water interchange occurs and flows through the reaction zones. Characteristics of overlying aquifers are:

1) Overlying sand aquifer occurs intermediately between the coal and overlying impermeable beds and contains various rocks including claystones and siltstone that were deposited under varying depositional environments. The most permeable unit is confined to stacked channel sands. It has moderately post-test high sulfate contents and high TDS.
2) Pre-test coal aquifer. This is a fracture-dominated, highly permeable aquifer. Potentiometric surface measurements indicate that groundwater flow is generally dictated by cleat fracture direction. It contains low sulfate contents but high Mg, HCO_3, and Na. Pre-test chemical character of this aquifer represents a bicarbonate system with high ionic activities.

There are two sources of pollutants in prematurely terminated UCG.

1) The cavity area and the surrounding high ash, tar and charcoal zone. Ash contains most of the organic, inorganic chemical species and mineral matter that was originally in the coal matrix. Groundwater migrating through the ash mobilizes soluble anions and cations. Compositional variabilities of Na, K, Ca, Mg, SO_4, HCO_3, CO_3, toluene, benzene and phenols in groundwater were statistically evaluated, but we shall discuss chemical parameters (organic or inorganic) that:
   a) have shown increased post-burn levels, such as SO_4, in coal aquifer monitoring wells.
   b) those such as COD, TOC, and Phenols that have decreased in concentration after gasification but are useful indicators of both redox conditions and organic pollutants in groundwater.
2) As hot gases (which are actually mixtures of gases and steam) migrate through fractures and fissures in the coal. Temperature differentials are created in areas remote from the cavity zone. These gases first react at high temperature with the rocks they are in contact with and second they condense as they cool to be dissolved later by the groundwater with which they equilibrate. Leaching of soluble salts may eventually be removed. Chemical reactions may occur at large distances from the gasifying chamber especially if the hydrologic system is fracture-dominated. At least three reactive gases, (SO_2, CO_2, N_2) initially predominate in the groundwater system. Contaminants originating from this type does not usually pose a serious problem as they are either ion-exchanged or absorbed by the fresh coal with which they are in contact. Mineral equilibrium conditions may be disturbed for some time.

CHEMICAL OXYGEN DEMAND (COD)/TOTAL ORGANIC CARBON (TOC)

The variability of Chemical Oxygen Demand, Total Organic Carbon, and Dissolved Organic Carbon for any sampling period is indicative of the compositional changes in groundwater. TOC is a measure of the total organic carbon (extractable carbon) and is a measure of the amount of organic carbon in groundwater. COD is a measure of that portion of organic material that is susceptible to oxidation by a chemical oxidant and is indicative of reduction capacity of an organic matter (Behi, 1982). COD, which is used to determine the amount of organic pollution, is empirically related to the heat of formation and estimates the amount of energy available for metabolic requirements of a microorganism. Variation in the ratio of COD signifies the amount of TOC potentially oxidizable to carbon relative to the total carbon present in the water. As an example, following data (Table 1) are shown for one coal formation well for the sampling periods shown. Table 1 portrays the ratio of COD/TOC.

TABLE I

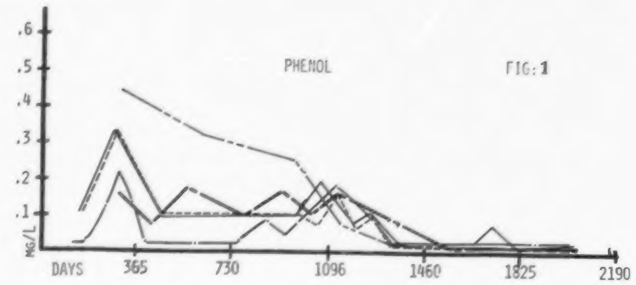
Parameter	Post-Burn Sampling Period	
	1	2
COD (mg/l)	11	11
TOC (mg/l)	4	3
DOC (mg/l)	4	4
COD/TOC ratio	2.25	3.67

It is obvious from the data above that, although low concentrations of COD and TOC are reported, sample 1 is more reducing than the subsequent sample. Low dissolved organics may be indication of a low tar formation, confirming perhaps, that the methenation was predominant reaction in most of the process wells. It is noted that the upper aquifer, as would be expected, shows small TOC, DOC, and COD variations. Data on COD/TOC ratios calculated for selected wells monitoring from overlying, sandstone aquifer, and coal aquifer for a period 5 years after the burn indicate that wells in the reaction zone show the highest ratios, followed by wells adjacent to the burn.

PHENOLS

A wealth of information, accumulated for the last few years on both experimental and field-oriented studies, are available in UCG literature. Published data on phenolic materials emanating from UCG indicate that phenols do not pose a long term contaminant problem (Dalton, 1978). Both experimental investigations and field evidence data indicate that phenolic compounds with concentrations as high as 3000 mg/l are immobilized a short distance (less than 100 ft.) from the gasification chamber (Walters and others, 1980). Coal is an effective adsorber of phenols in aqueous solutions. (Fig. 1)

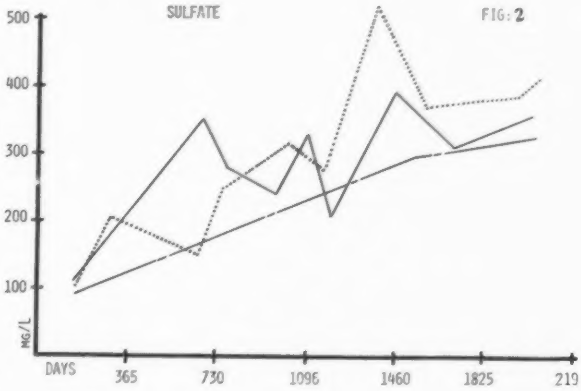
Phenols can be removed efficiently by oxidative chemical means with or without bacterial action. Except for chemical oxidation all other phenal removal processes always leave some residuals. Selective methylation (CH_4) of the hydroxyl group (OH) or phenols result in



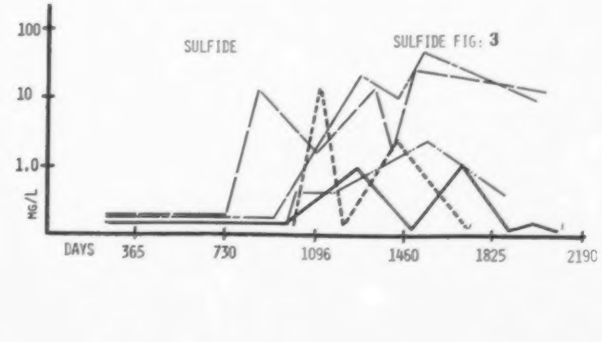
toluene formation. It is to be emphasized that the reason why phenols are a major constituent of UCG is that lignin is a major component of woody coal precursors and yield phenols when thermally decomposed. Because of the OH functional group that is attached to phenols, this, under proper chemicals, dissociates into a weak acid and an anion (Glaze, 1984).

SULFATE

The coal formation shows a predominate bicarbonate type of water, in contrast with the overlying sand aquifer, which carries a predominately sulfate type. After gasification was shut down, sulfate increased in concentration in burn zone wells and in other wells monitoring from the cavity, as shown in Fig. 2. Other coal aquifer monitor wells have shown slight sulfate increases over the pre-test levels.



Although sulfides have shown up in the overlying sand aquifer, appreciably higher amounts of dissolved sulfides are indicated for the coal aquifer (Fig. 3). The increased sulfide concentration after gasification is attributed to the reduction of sulfate. Sources of high post-burn sulfate can be ascribed to:



1) External source of sulfate probably as a result of hydraulic communication established between the overlying sand aquifer and the coal aquifer.
2) Oxidation of pyritic and organically bound sulfur in coal during early stages of gasification. Due to large volumes of oxygen that had been injected into the coal formation, oxidation of iron sulfides would have occurred. Early post burn water analyses contain consistently higher concentrations of iron, calcium, conductivity, and sulfate.

SO_2 is produced during gasification. This gas reacts with excess water and steam in the reaction zone to form sulfuric acid, which dissociates into hydrogen ions and sulfate under active burn conditions. Sulfates that remain (sulfate reduction is both pH and Eh dependent) is further reduced in an acid media by hydrogen sulfide gas to form native sulfur.

$$3H_2S + SO_4^{-2} + 2H^+ \rightarrow 4S^0 + 4H_20$$

One source of hydrogen ions for the reaction is the reduction of ferrous iron by hydrogen sulfide. This reaction, which indicates precipitation of iron sulfides, can be written as follows:

$$Fe^{+2} + H_2S \rightarrow FeS + 2H^+$$

In an oxygen deficient post-burn environment, oxidation of organic matter by an aerobic bacteria can occur, using nitrates as a source of oxygen (electron acceptor). If nitrates are consumed in the natural environment, degradation continues by an aerobic bacteria, utilizing sulfate as the oxidant, according to the following reaction scheme:

$$(CH_2O) + SO_4 \rightarrow CO_2 + H_2O + H_2S$$

Aerobic bacteria may use this reduction both for energy and as a source of molecular oxygen. Sulfate reduction in the post-burn coal groundwater is manifested by the abundant H_2S and ubiquitous reduced sulfur, probably dominated by HS^-. Acidity is produced by a bacterially mediated oxidation and by reduction of ferrous iron by hydrogen sulfide.

Analytical data shows that the coal contains reduced sulfur as total sulfide sulfur. This might have been formed in two ways:

1) from consendates during gasification processes. Analyses on gas consendates showed that high levels of sulfide sulfur were present.
2) as a result of in situ sulfate reduction. This redox reaction is controlled by pE activity and bacterial action, which facilitates an electron transfer during oxidation of the organic nutrient.

In order to empirically define the magnitude of the observed reducing conditions, pE, a relative electron, were calculated for the system $H_2S - HS^- - SO_4^2$ for the coal aquifer. pE values were calculated from molar concentrations of HS^- and SO_4^{-2}. Computed pE values were then converted to Eh values. The change of pE in groundwater is related to the amount and reactivity of decomposed organics, and reduction of sulfate is controlled by electron activity.

Fig. 4 is a plot of calculated values of Eh and laboratory pH values for various wells. It can be gleaned from this plot that groundwater pertaining to $H_2S - HS - 1 - SO_4^{-2}$ system has not reached equilibrium.

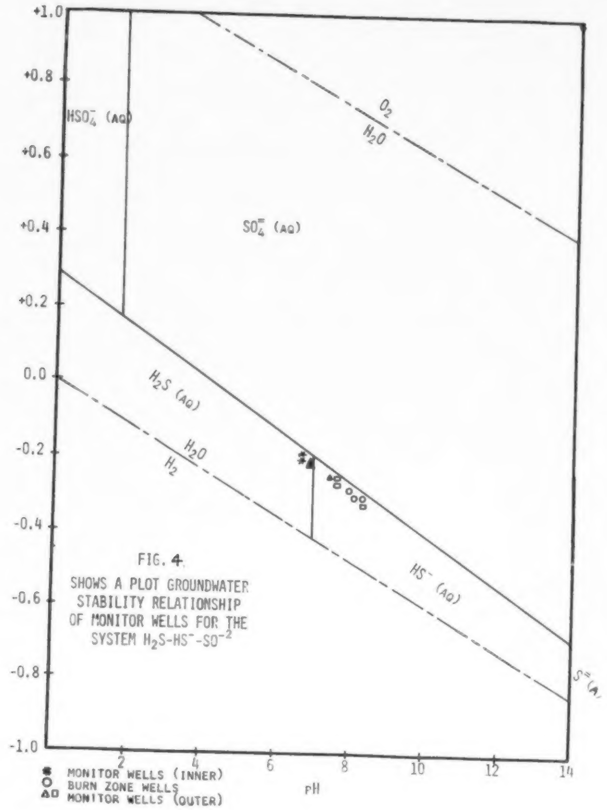


FIG. 4

SHOWS A PLOT GROUNDWATER STABILITY RELATIONSHIP OF MONITOR WELLS FOR THE SYSTEM $H_2S-HS^--SO^{-2}$

HYDROCHEMICAL MINERAL STABILITY RELATIONSHIPS

Thermodynamic activity equilibrium on chemical data obtained for two sampling periods were calculated. For the high sulfate water (582 mg/l), gypsum (log K = −4.61, log Q = −5.79) were found to be under-saturated, indicating probable gypsum disssolution, while calcite shows over-saturation (log K = −8.37, log Q = −7.66). For low sulfate concentration (38mg/l) the same saturation equilibrium trend was observed, in which groundwater system was under-saturated with respect to gypsum and over-saturated with respect to calcite. The two samples with large difference in sulfate concentrations attest to the fact that gypsum is under-saturated and is probably dissolving. So, although probable bacteria reduction of sulfate occurred which resulted in the lower sulfate contents for the later sampling dates, gypsum is thermodynamically unstable in this well.

CONCLUSIONS

During UCG processes, thermochemical reaction of coal produce volatiles that migrate through the permeable formation zones, organic and inorganic residuals that remain in decomposed coal matrix. Organic contents in groundwater eventually return to baseline levels. Of all the inorganic ionic species mobilized, sulfate persists in groundwater in levels exceeding background concentration. The elevated sulfate contents is in part due to gypsum dissolution of a result of interaction of activated groundwater with calcium sulfate-bearing stratigraphic units. Calculation of thermodynamic equilibrium calculations indicate that calcite is over-saturated while gypsum is under-saturated in post-test groundwater.

COD/TOC ratios are useful indicators of the amount of oxidizable organic content and the magnitude of reduction capacity of the prevailing groundwater system. Calculated Eh and laboratory-derived pH values were plotted for $H_2S - HS^- - SO_4^{-2}$ system to show empirically the redox conditions and equilibrium stability relationships of different sulfur species. Future comparison of this Eh-pH plot with changing values with time, should indicate equilibrium trends in the stability field of sulfur components.

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THE DISTRIBUTION OF SELECTED TRACE ORGANICS IN THE LEACHATE PLUME OF A MUNICIPAL LANDFILL

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ABSTRACT

In the leachate plume of the municipal landfill of North Bay, Ontario, the distribution of trace organics, such as petroleum-derived aromatic hydrocarbons, chlorinated solvents, and aliphatic and aromatic acids, has been analyzed. Chloride (Cl^-) was used as a conservative tracer. The input into the 800 m long plume was evaluated at a multilevel observation well near the boundary of the landfill by analyzing 5 samples over a two-year period. The Cl^- concentration remained relatively constant (± 20%) relative to the aromatic hydrocarbon concentrations, which varied by almost an order of magnitude. However, the concentration ratios of the individual hydrocarbon compounds remained relatively constant. The measured concentrations were in the low μg/L range, approximately three orders of magnitude below the solubility limit of the compounds. Trichloroethylene (Cl_3EY) has been detected at the μg/L level beneath the plume, at the bottom of the aquifer, but not in the anaerobic plume. 1,4-dichlorobenzene was detected throughout the plume indicating both stability and mobility of this compound under anaerobic conditions. The petroleum-derived aromatic hydrocarbons showed a mixed behavior, suggesting that selective and variable attenuation may have been effective.

INTRODUCTION

At the municipal landfill of North Bay, Ontario, which has been in operation since 1962 and receives domestic, commercial, and small quantities of industrial wastes, organic groundwater contamination by leachate has been investigated by analyzing water samples from multi-level observation wells over a period of two years. The North Bay site has been selected for this detailed investigation because (i) previous studies conducted by the Department of Earth Sciences of the University of Waterloo (Cherry et al., 1981; Cherry, 1983) have delineated the shape and the major geochemical features of the plume, (ii) an extended network of multi-level observation wells was available in place, (iii) the aquifer was shallow and samples could be obtained with relative ease, and (iv) a preliminary investigation has indicated emanation of trace organics from the landfill (Reinhard et al., 1984).

The landfill is situated on glacio-fluvial sandy deposits which comprise occasional gravel and silt lenses. At the bottom, the aquifer is confined by a discontinuous layer of silty-sandy glacial till deposited on biotite gneiss. The plume, first documented by Cherry et al. (1981), appeared to be at a relative steady state. All major ions except K^+ and NH_4^+ had broken through to the leachate springs 800 m downstream of the landfill (Fig. 1). At some levels of observation well G, the Cl^- concentration exceeded 800 mg/L. At AAA, the Cl^- concentrations were lower and ranged from 100 to 200 mg/L, presumably attenuated by hydrodynamic dispersion. Throughout the plume, conditions appeared highly reduced as indicated by low NO_3^- levels and by the abundance of NH_4^+, Mn(II), and Fe(II) (Cherry, 1983), and methane (King, 1983).

Here we report on temporal and spatial variations of selected trace organics including trichloroethylene (Cl_3EY), naphthalene, 1,4-dichlorobenzene (1,4-DCB), ethylbenzene, and o-xylene. These compounds were selected because they represent characteristic biogeochemical behaviors. Cl_3EY has been shown to be degraded anaerobically by sequential dehalogenation (Parsons et al., 1984). However, Cl_3EY appears to be stable under aerobic conditions (Schwarzenback et al., 1983). 1,4-DCB behaves in the opposite way. It has been found to degrade under aerobic conditions in the laboratory (Bouwer and McCarty, 1982) and in field systems (Schwarzenbach et al., 1983), but appears to be stable under anaerobic conditions (Bouwer, 1982; Bouwer and McCarty, 1982). Aromatic hydrocarbons, including toluene, alkylbenzenes and naphthalene, have been found to be biologically removed in aerobic groundwater recharge systems (Roberts et al., 1980; Schwarzenbach et al., 1983) and in biological laboratory columns (Kappeler, 1976; Bouwer, 1982; Bouwer and McCarty, 1984). Under anoxic conditions, aromatic hydrocarbons are assumed to persist (Schlegel, 1981) This was confirmed for ethylbenzene, naphthalene, and styrene in methanogenic laboratory columns (Bouwer, 1982).

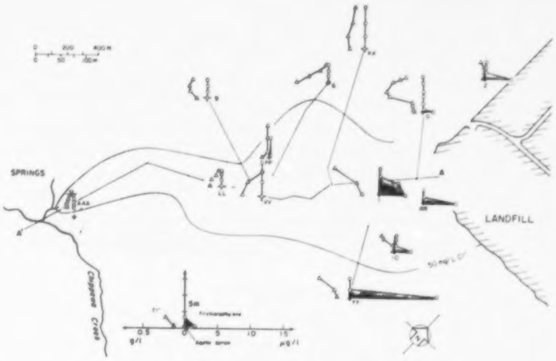

Figure 1. Municipal Landfill at North Bay, Ontario: Plume boundary identified by the 50 mg/L Cl^- contour, and vertical profiles of Cl^- and trichloroethylene. Sampling dates: 6/14/82, AAA, LL; 7/11/82, G; 9/1/82, KK, VV, 6, 9; 9/14/82, PP; 8/17/82, YY, 1, 2, 10; 10/17/82, RR.

METHODS

Samples were taken using multi-level sampling devices with the lowest sampling tube extending to the bottom of the aquifer (Cherry et al., 1983). Samples were air freighted to the Stanford Water Quality Research Laboratory in cooled containers and stored at 4°C until analysis.

Volatile chlorinated organics were analyzed using a pentane-extraction method developed by Henderson et al. (1976), purgeable aromatics were analyzed using the closed-loop purge-and-trap method developed by Grob and Zurcher (1976) using the mass spectrometer as a specific detector. Carboxylic acids were analyzed by liquid-liquid extraction using methylene chloride, followed by methylation with diazomethane and gas-chromatographic mass-spectrometric (GC/MS) analysis using a Finnigan 4000-INCOS GC/MS system (Reinhard et al., 1984).

RESULTS AND DISCUSSION

Trichloroethylene

At the wells indicated in Fig. 1, vertical profiles of Cl^- and Cl_3EY were measured. Near the landfill, the Cl^- concentrations which define the leachate plume were greatest in the upper half of the aquifer, but relatively low in the bottom layers of the aquifer. With distance, however, the plume appeared to sink to the bottom of the aquifer as is evident from the downstream Cl^- profiles. Cl_3EY did not conform to the Cl^- behavior. The Cl_3EY concentrations in the vicinity of the landfill were greatest at the bottom of the aquifer, where the Cl^- concentrations were lowest. The elevated concentrations at the bottom of the aquifer may arise from liquid Cl_3EY which has sunk to the bottom of the aquifer as Cl_3EY is heavier than and immiscible with water. Hence two-phase flow of chlorinated solvents may be a significant process that needs to be considered when the impact of landfills on ground water is evaluated. To date, there exist only laboratory studies on this phenomenon (Schwille, 1981).

Cl_3EY detected at the bottom of the aquifer may have formed a separate plume, which dispersed downstream into the anaerobic leachate plume. Thus the Cl_3EY may have been transported from beneath the chloride plume, where conditions are presumably aerobic and unfavorable for biological transformation, into the anaerobic chloride plume, where biological transformation is possible. Further downstream, Cl_3EY was generally absent or detected only at trace levels. Biologically mediated dehalogenation of Cl_3EY and of other halogenated aliphatics has been demonstrated in the laboratory studies under methanogenic conditions (Bouwer, 1982; Bouwer and McCarty, 1983; Parsons et al., 1984).

1,4-Dichlorobenzene and Naphthalene

Figure 2 depicts the temporal variations of Cl^-, 1,4-DCB, and naphthalene at three representative observation points during the two-year study period. At well G, the concentrations of naphthalene and 1,4-DCB fluctuated by almost an order of magnitude, whereas the Cl^- concentration remained relatively constant. The relatively constant Cl^- levels support the assumption that the plume is at a virtual steady state with respect to the major inorganic ions. Remarkably, the variations in the concentration of naphthalene and 1,4-DCB corresponded very closely, suggesting that these two compounds are released from the same source. The measured concentrations of both naphthalene and 1,4-DCB were significantly below their respective solubility limits, which are 30 mg/L for naphthalene and 79 mg/L for 1,4-DCB. This suggests that these compounds are released from a hydrocarbon pool which is saturating the water with mixture of hydrocarbons of constant composition.

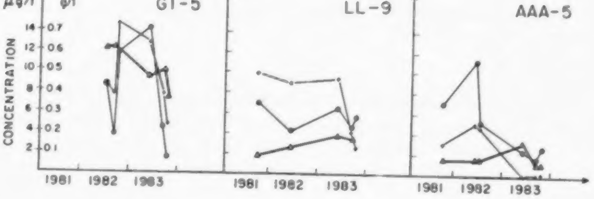

Figure 2. Temporal variations of 1,4-dichlorobenzene, naphthalene, and Cl^- at G1-5, LL-9, and AAA-5.

The concentrations of compounds which preferentially partition into an organic phase is proportional to their solubility limit and their concentration in the organic phase:

$$C^i(H_2O) = X^i(\text{pool})\, C^i_s(H_2O)$$

where $C^i(H_2O)$ is the equilibrium concentration of compound i in water, $C^i_s(H_2O)$ is the solubility limit, and X^i(pool) is the mole fraction of compound i in the "pool" (Stumm and Morgan, 1981). To explain the great variations shown in Fig. 2, a non-equilibrium situation or varying degrees of dilution subsequent to water saturation must be assumed. In previous analyses (Reinhard et al., 1984), the sum of all the aromatic hydrocarbons in water sampled at piezometer G were significantly higher (approximately 2 mg/L), relatively close to the values measured in water saturated with diesel fuel (Zurcher and Thuer, 1978). Hence, different degrees of saturation appear to occur at different wells and at different times. The fact that the concentration ratios of the various pollutants remain constant is of great practical significance for evaluating pollutant behavior, as is exemplified below with ethylbenzene and o-xylene.

At LL-9, the concentrations of both compounds were generally lower and the concentration variations were damped as would be expected from the combined action of dispersion and retention (Roberts et al., 1982). However, further downstream at AAA, a significantly different behavior was noted. Naphthalene was reduced to trace levels during 1983, even though Cl^- remained relatively constant. 1,4-DCB decreased as well but not to the same extent, remaining above the 2 μg/L level. This drop in naphthalene concentration was surprising and, perhaps, suggests a change from a biogeochemical regime which inhibited degradation to one that favors degradation of this compound. However, other factors, which may cause such a behavior such as variations in input concentrations, cannot be ruled out at this time.

Ethylbenzene and o-Xylene

Figure 3 indicates vertical profiles of ethylbenzene and o-xylene at various points along the centerline of the plume and also indicates the shape of the plume delineated by Cl^-. Ethylbenzene and o-xylene are both components of petroleum hydrocarbons which are released at about equal concentrations, as indicated by the close correspondence of the vertical profiles at G. Interestingly, they seem to be retarded to varying degrees in spite of their similar physico-chemical characteristics. (The log of the octanol-water partition coefficients of ethylbenzene and o-xylene are 3.15 and 2.77, respectively.) o-Xylene appears to be attenuated to a significantly greater extent than ethylbenzene, which is present at greater concentrations at most observation points downstream of G. The reason for this apparently selective attenuation may be due to biogeochemical regimes which favor the removal of o-xylene over ethylbenzene, or, due to selective physico-chemical adsorption processes. Subsequent analyses have indicated that the profiles change significantly with time, yet, the greater attenuation of o-xylene relative to that of ethylbenzene seems to persist. More work is needed to understand the behavior of these compounds under the prevailing biogeochemical conditions.

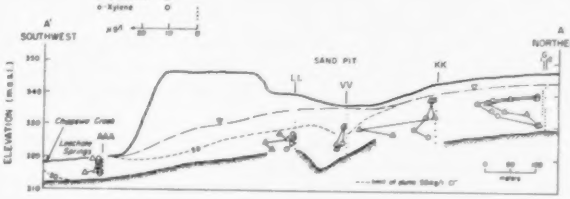

Figure 3. Vertical concentration profiles of ethylbenzene and o-xylene. Boundary and plume identified by the 50 mg/L Cl^- contour along cross section A-A'.

SUMMARY AND CONCLUSIONS

Spatial and temporal distribution of trace organics in landfill leachate plumes and analysis of the product spectrum has given valuable insight into the significance of physical, physico-chemical, and biological processes affecting the fate of trace organics in the subsurface environment. The distribution of Cl_3EY has suggested that two-phase flow may be a significant process affecting the distribution of chlorinated solvents in landfills. A significant practical consequence of this observation is that Cl^- is an unreliable tracer for establishing the lower boundaries of the trace organics plumes.

Aromatic hydrocarbons are released at a varying rate, but at a relatively constant concentration ratio. Release of aromatic hydrocarbons may be controlled by a partitioning-like process between the mobile water and a stagnant organic pool. The reported stability of 1,4-DCB under anaerobic degradation has been confirmed under field conditions. Non-chlorinated aromatic hydrocarbons appeared to be attenuated to varying degrees under the prevailing anaerobic conditions. With the presently available data, however, it cannot be conclusively established whether the observed attenuation is due to biological or physio-chemical processes.

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FACTORS INFLUENCING THE SURVIVAL OF VIRUSES IN GROUND WATER

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ABSTRACT

Although ground water accounts for only approximately 20% of the nation's water supply, 50% of all waterborne disease outbreaks in the United States is due to contaminated ground water. More than half of these cases of illness are believed to be caused by enteric viruses. Little, however, is known about the persistence of these organisms in ground water. This study investigated the persistence of a bacterial virus, MS-2, and two animal viruses, Poliovirus-1 and Echovirus-1, in ground water samples collected from throughout the United States. Each virus was inoculated into separate, sterile polypropylene containers of ground water and incubated in the laboratory at the characteristic temperature of the source. Duplicate experiments were performed using the natural ground water and ground water that had been filtered to remove bacteria. Subsamples were assayed at predetermined intervals over a 30-day period. Several chemical characteristics were determined for each ground water tested. Ground water temperature was the only water characteristic found to be significantly correlated with the persistence of all three viruses. There were no consistent trends found in the ability of any of the viruses to persist in the presence or absence of the indigenous bacteria.

INTRODUCTION

Viruses are ultramicroscopic particles, many of which are capable of infecting humans. Viruses which can replicate in the gastrointestinal tract, and thus be excreted in fecal material, are termed enteric viruses. Over 100 different types of enteric viruses can be found in domestic sewage (Gerba, Wallis, and Melnick; 1975); the most widely studied of these are members of the Picornavididae family. This family includes polioviruses, echoviruses, coxsackieviruses A and B, and hepatitis A virus. Diseases caused by these viruses include diarrhea, fever, meningitis, paralysis, and infectious hepatitis.

It has been estimated that 65% of the documented outbreaks of waterborne disease in the United States from 1946 to 1977 can be attributed to illness of probable viral etiology (Gerba, 1983). Over one-half of all waterborne disease outbreaks in the United States are caused by the consumption of untreated or inadequately treated ground water. Overflow or seepage of sewage from septic tanks or cesspools was responsible for 43% of the outbreaks caused by contaminated ground water (Craun, 1984). The potential for viruses present in sewage to contaminate ground water is determined by two factors: migration through the soil and persistence in the subsurface. Migration and persistence are controlled by three interacting factors: the climate, the soil type, and the virus type (Gerba, 1983). The factors affecting the fate and transport of viruses in soils have been studied (Sobsey, 1983). Little, however, is known about the persistence of viruses in ground water.

The purpose of this investigation was to study the factors influencing virus persistence in ground water. Specifically, the objectives were:

1) To investigate the influence of temperature of virus persistence in ground water.
2) To determine the effects of chemical and physical characteristics of several water samples on virus persistence.
3) To determine the effects of the indigenous bacteria on virus persistence.
4) To gain information which can be used as criteria in developing a model to predict safe distances between drinking water wells and sources of potential contamination, such as septic tanks and sites of land application of waste.

MATERIALS AND METHODS

Ground water samples were obtained from several different sites (Table 1). The samples were collected aseptically in sterile polypropylene bottles and packed on ice for transport to the laboratory. Temperature was measured at the time of collection. Prior to inoculation with viruses, the samples were analyzed for several chemical and physical parameters according to standard methods (APHA, 1980; USEPA, 1974). These included pH, turbidity, ammonia, nitrate, total dissolved solids; and calcium, magnesium, and total hardness.

TABLE 1. SAMPLE COLLECTION SITES

SAMPLE	TEMPERATURE (°C)	SITE DESCRIPTION
WISCONSIN	12	DOMESTIC DRINKING WATER WELL 50 FEET DEEP
ARIZONA	23	DRINKING WATER WELL
TUCSON	23	MONITOR WELL, 1200 FEET DEEP
TEXAS 1	13	WELL IN FIELD RECEIVING RECLAIMED WATER, 25 FEET DEEP
TEXAS 2	13	WELL IN FIELD RECEIVING RECLAIMED WATER, 23 FEET DEEP
CALIFORNIA 1	18.5	WELL RECEIVING GROUND WATER CONTAINING 10% RECLAIMED WATER
CALIFORNIA 2	17	NEGATIVE CONTROL WELL
NEW YORK 1	12	MONITOR WELL NEAR LANDFILL
NEW YORK 2	12	MONITOR WELL NEAR LANDFILL
NORTH CAROLINA 1	14	MONITOR WELL NEAR SPECTIC SYSTEM, DEEP AQUIFER
NORTH CAROLINA 2	14	MONITOR WELL NEAR SEPTIC SYSTEM, SHALLOW AQUIFER

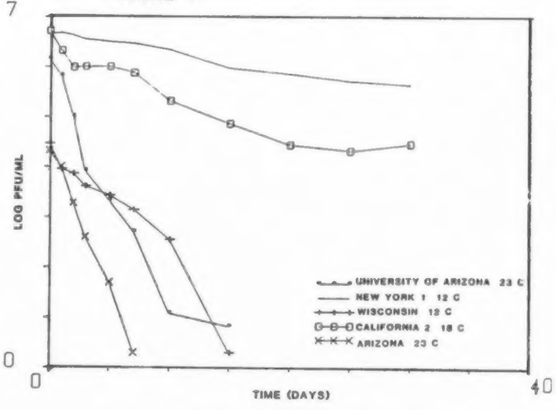
Each of the three viruses was inoculated into separate sterile, polypropylene containers containing a ground water sample. Duplicate tubes containing ground water which had been filtered to remove bacteria were also inoculated. The tubes were incubated at the in situ ground water temperature. One-ml subsamples were withdrawn on days 0,1,2,3,5,7,10,15,20,25, and 30 and assayed to determine the number of viruses present. The MS-2 phage was assayed using the agar-overlay plaque technique of Adams (1959); *E. coli* ATCC 15597 was used as the bacterial host. The number of animal viruses was determined by the enumeration of plaques formed in Buffalo Green Monkey kidney cells under an agar overlay.

Multiple regression analysis of the data was performed using the computer program "REGRAN" (Veldman, 1967).

RESULTS AND DISCUSSION

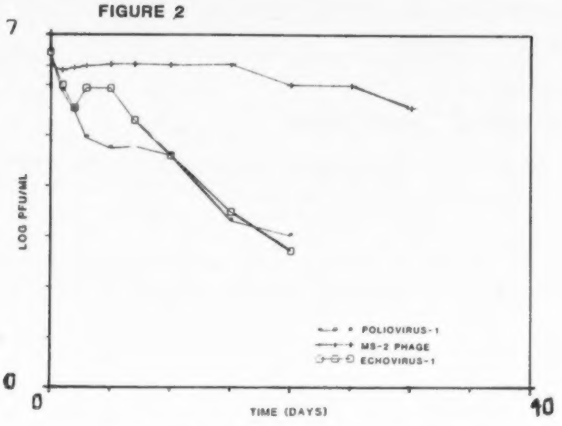
The persistence of MS-2 phage in five of the ground water samples is presented in Figure 1. A comparison of the behavior of all three

FIGURE 1



PERSISTENCE OF MS-2 PHAGE IN GROUND WATER SAMPLES

FIGURE 2



PERSISTENCE OF VIRUSES IN NORTH CAROLINA 1 GROUND WATER SAMPLE

viruses in the North Carolina 1 water sample is shown in Figure 2.

Multiple regression analysis of the data revealed that temperature was the only measured water characteristic that was significantly correlated ($p = 0.05$) with the persistence of all three viruses. The correlation was a negative one: as temperature increased, virus persistence decreased. The presence or absence of bacteria was not significantly correlated with the virus persistence in all water samples. There were, however, differences in virus behavior in some water samples between the filtered and non-filtered waters. In some water samples, the viruses persisted for a longer period of time in the filtered water; in other water samples, the opposite results were observed. The role of bacteria in affecting virus persistence in ground water needs further investigation.

The persistence of the viruses in the eleven water samples is presented in Table 2 as the number of days to achieve a one log (90%) reduction in virus titer. At low temperatures, such as 12 C, 25 days were required for a 90% reduction in the original titer. Depending on the characteristics of ground water flow in the area, this could be long enough for viruses introduced into the subsurface to contaminate potable water, and potentially transmit human disease.

TABLE 2. PERSISTENCE OF VIRUSES IN GROUND WATER SAMPLES

SAMPLE	TEMPERATURE (°C)	DAYS TO 1 LOG REDUCTION IN TITER MS-2	POLIOVIRUS-1	ECHOVIRUS-1
Wisconsin	12	10.8	16.6	15.2
Arizona	23	3.1	1.5	1.6
Tucson	23	1.7	2.8	5.3
Texas 1	13	13.0	27.5	7.3
Texas 2	13	8.8	7.3	12.7
California 1	18.5	12.3	5.4	6.6
California 2	17	13.3	12.3	11.0
New York 1	12	29.1	28.8	18.5
New York 2	12	27.0	19.3	19.7
North Carolina	14	10.6	7.3	5.0
North Carolina	14	10.6	8.8	5.8

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REMOVAL OF IRON AND MANGANESE FROM GROUND WATER WITH THE VYREDOX Ⓥ METHOD

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ABSTRACT

Water systems with wells drawing ground water containing soluble iron and manganese can have production capacity losses, transmission capacity losses and consumer complaints about odor, staining and taste.

Vyredox is a method for removing iron and manganese from ground water at the source, in the ground, before the water is drawn to a well. It works by raising the redox potential in the ground around a well with periodic recharges of aerated water using specially engineered conditioning equipment and recharge wells. The oxygen in the recharge water acts as a catalyst to begin a biochemical reaction that transforms iron and manganese from their soluble form to insoluble compounds that are kept in the ground away from the well.

Vyredox plants have been in operation world wide since 1955. Since 1979, in the U.S., pilot studies have been conducted at 20 sites. Full scale plants have been completed at three sites and are under construction at three more. Vyredox has proved applicable and economical in varied settings for a wide range of raw water quality.

INTRODUCTION AND BACKGROUND

Iron and manganese are found in many well water supplies. They impart an unpleasant taste to the water and turn it red or black when they begin to settle out. Water consumers complain when iron and manganese deposits stain fixtures and laundry. Iron and manganese deposited in pipes and on well screens reduce hydraulic capacity increasing operation and maintenance costs. Deposits in storage reservoirs and elsewhere in water distribution systems interfere with disinfection and can harbor harmful organisms.

Iron and manganese can be chemically suspended, at least temporarily, if concentrations are not too high; however, removing the metals solves iron and manganese problems. The metals can be removed above ground with filtration plants or in-ground as with the Vyredox Method. Only in-ground treatment prevents well capacity loss from deposition of iron and manganese on well screens.

In 1955, two Finish well drillers (Villi and Yuri Rejonen) decided to improve the water quality in a well containing a high concentration of iron by storing pure water from a nearby well in it during off-peak days. When they pumped the poorer quality well, they found they could pump more water than was added. Successive recharges improved quality even more. They named their invention the Vyredox Method Ⓥ; by combining the initials of their first names with "redox", which is the chemical parameter controlling iron and manganese concentrations in water. Vyredox has undergone considerable refinement in theory and practice since 1955, but the principle is unchanged.

IRON AND MANGANESE IN GROUND WATER

Iron is the fourth and manganese the twelfth most abundant element in the earth's crust. On the average, a cubic yard of the earth's crust contains 200 pounds of these metals, yet not all ground water contains them. Iron and manganese are insoluble and not found in water if the water is oxidized. As water passes through organic matter, such as is found in swamps, forest beds and the bottoms of some surface water bodies, or comes into contact with certain minerals, it becomes less oxidized or in other terms, more reducing (Drever, 1982).

The measure of whether a water is oxidized or reduced is called its redox potential or Eh. Figure 1 shows the occurrence of soluble and insoluble iron and manganese as a function of Eh and pH. When the combination of Eh and pH of a water falls in the lower portion of the figure, both iron and manganese are soluble. In the middle portion, iron is insoluble, but manganese can still be found in the water. In the top portion of Figure 1 both iron and manganese are insoluble (Drever, 1982). Vyredox works by raising the redox potential and transforming iron and manganese from the soluble to the insoluble forms.

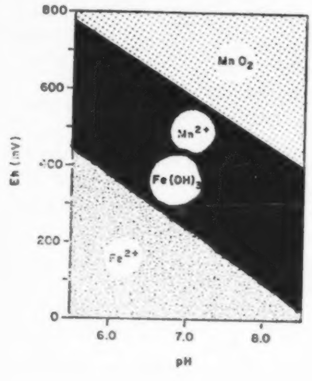

FIGURE 1

SOLUBLE (Fe^{2+}, Mn^{2+}) AND INSOLUBLE [$Fe(OH)_3$, MnO_2] IRON AND MANGANESE AS FUNCTIONS OF THE VARIABLES pH AND Eh

IN-GROUND IRON AND MANGANESE REMOVAL BY THE VYREDOX METHOD

With Vyredox, redox potential in the aquifer is raised by creating a treatment zone in the ground around a well. Production from a well being treated is periodically stopped when a predetermined volume has been pumped. While production is stopped, water is drawn from another well or the water distribution system, conditioned in an aeration-degassing plant and diffused through several recharge wells surrounding the production well. After a 4-hour contact time, production can be resumed until the preset volume indicating need for the next recharge is reached. This recharge cycle is required every few weeks or months depending on usage and system efficiency.

The treatment zone formed by a recharge cycle is shown in Figure 2. The original Eh, 100 mV on the figure, is raised to a level of 200 to 600 mV. Water pumped from the well is free of iron and manganese.

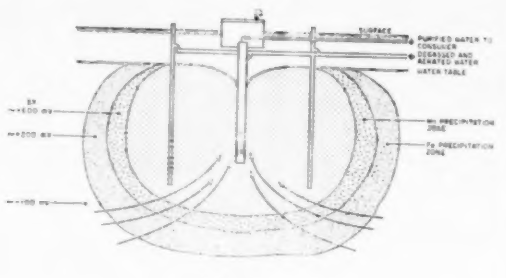

FIGURE 2
AQUIFER CROSS SECTION
VYREDOX METHOD
IRON AND MANGANESE PRECIPITATION ZONE

More water is treated than is contained in the treatment zone. If that were not so, only a volume equal to that recharged could be pumped. In practice, the recharge volume has been as little as 4 percent of the production volume. Research indicates that there are harmless microorganisms in the ground that help oxidize the iron and manganese and render them insoluble (Kucera, 1957; Mallard, 1981). The oxygen in the aerated water raises the Eh which acts as a catalyst to activate the microorganisms which then begin biochemical oxidation. As the iron and manganese are oxidized, electrons are released, maintaining the elevated Eh level and precipitating the iron and manganese, even in the absence of oxygen. When a certain amount of precipitation has taken place, the catalyzed reaction stops until the Eh can be artifically elevated again.

As water with iron and manganese enters the treatment zone, these elements are removed at the outer edge. As pumping continues, the edge of the treatment zone slowly collapses toward the center at a rate relative to the amount of iron and manganese removed, until recharge is required again (Hallberg, 1976).

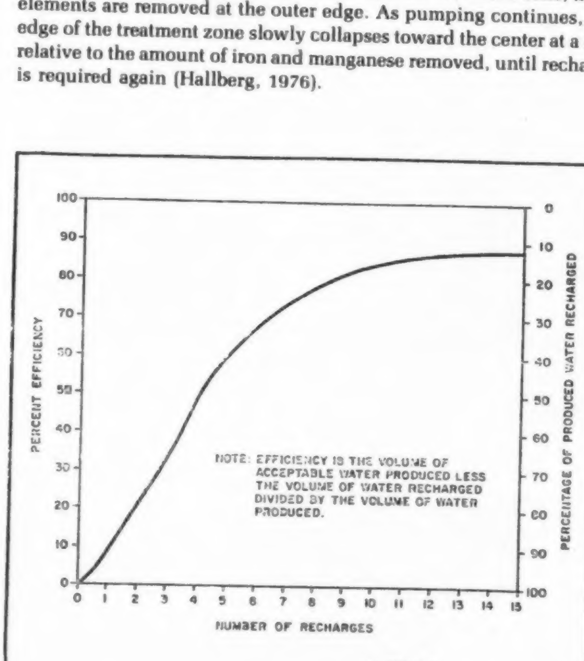

FIGURE 3
TYPICAL TREND IN EFFICIENCY vs. NUMBER OF RECHARGES

An efficient treatment zone develops during a period of acclimation. The initial activity of oxidizing organisms is low in a reducing environment. As illustrated on Figure 3, a system will typically reach peak efficiency in 10 to 15 cycles of recharge and production. At that time, growth matches decay and biochemical activity is at a stationary phase.

FACILITY DEVELOPMENT

Facility development is a combination of construction and evaluation. Proper function of the unseen process must be evaluated indirectly with geological investigation and geochemical analyses before and during construction.

Evaluation begins with review of water quality data, space for facilities, aquifer flow patterns, mineralogy, and availability of recharge water. If Vyredox appears applicable, a pilot study is conducted to determine feasibility. A mobile Vyredox plant is used to recharge water directly into the production well being evaluated. Produced water is analyzed to evaluate reductions in iron concentration and the trend in quantity of recharge as a percentage of production, If iron is reduced to below 0.30 mg/l and the percentage of produced water used for recharge declines with successive cycles, the test is considered successful.

The size and dimensions of the recharge zone are determined based on pilot data and geologic investigation. The recharge zone must be large enough to allow treatment contact time, must consider aquifer flow, and provide adequate room for storage of deposits. The size of the zone is usually such that the soil pore space used to store the precipitated iron and manganese will not be filled up for hundreds of years (Hallberg, 1976). Therefore, Vyredox does not reduce the aquifer permeability during the life of the well.

Constructionbegins with installation of recharge wells. They are usually gravel-packed wells smaller in diameter than production wells but with longer screens. They are initially located based on the size and dimensions of the recharge zone design, but the locations often are adjusted based on evaluation during drilling. When the recharge wells are developed they are fitted with air release valves, throttling valves, and protective covers, and then they are piped to the aeration-degassing (A/D) plant.

The aeration-degassing plant is an automatic skid mounted unit designed for Vyredox. It has few moving parts and is easily maintained. Air is aspirated using the flow of water through the system thereby increasing the dissolved oxygen content of the water. A small centrifugal booster pump provides pressure of about 10 psi for distribution of the recharge water. Figures 4 and 5 illustrate well locations, piping arrangements and aeration-degassing equipent for the Vyredox plant in Seekonk, Massachusetts. Because operation of the plant is intermittent, one unit can treat several wells in a well field as shown in Figure 4.

Following construction the plant is started up over a period of six or more weeks. The controls are programmed and the equipment is debugged. Geochemistry is monitored to attain optimum recharge water distribution and maximum efficiency.

The cost of a Vyredox facility varies depending on raw water quality, aquifer characteristics, production rate and time required for start-up. Table 1 presents costs for plants completed in the U.S. to date. Annual treatment costs including operating costs plus capital costs amortized over 20 years at 10 percent amount to $21,203 to $45,470 per year. Costs are kept low because: flow space requirements are small, the equipment is automatic and runs intermittently, no sludge is produced and no chemicals are used. Savings are realized by reduction in well maintenance due to prevention of well screen plugging. In the oldest U.S. plant in Pembroke, Massachusetts well rehabilitation frequency and cost have been reduced in direct proportion to the reduction in iron concentration.

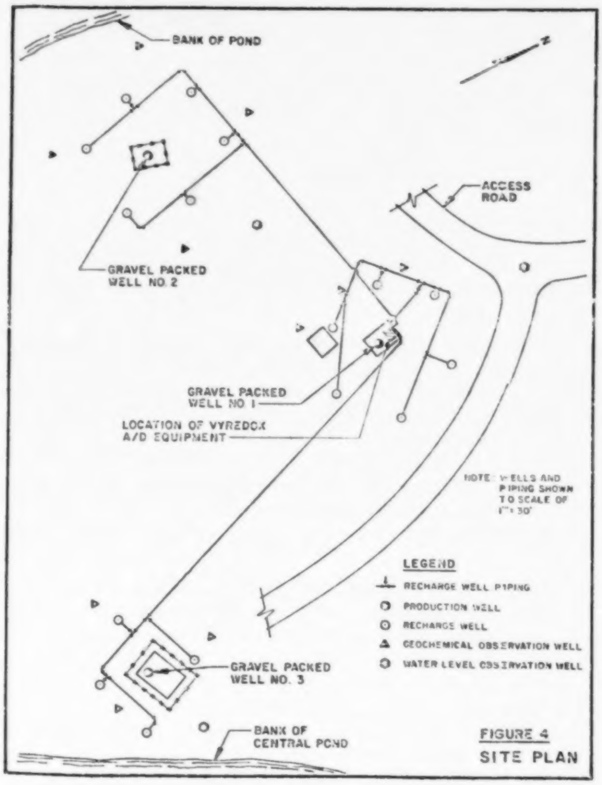

FIGURE 4
SITE PLAN

TABLE 1

VYREDOX COST DATA

	Date Completed	Capital Cost (1)	Annual Operating Cost (2)	Equivalent Annual Cost (3)	Production Capacity MGD
Pembroke, MA	June 1979	$150,000	$ 3,578	$21,203	0.58
Seekonk, MA (GP-1)	July 1983	$284,000	$12,100	$45,470	1.0
Endicott, NY	Dec. 1983	$270,000	$ 6,178	$37,903	2.0

(1) Capital cost is total project cost of completed plants including pilot work.

(2) Operating cost includes power, recharge well maintenance, equipment maintenance, and plant monitoring.

(3) Equivalent annual cost is operating cost plus capital cost X 0.1175 (20-year note at 10% interest).

OPERATING AREA

Tables 2 and 3 represent Vyredox operating data. Since 1978 pilot studies have been conducted at 20 sites in North America in varied geologic settings including unconsolidated aquifers of glacial, alluvial and coastal plain origin. Seventeen of the 20 have been successful enough to recommend permanent facilities. All studies in glacial and alluvial formations have been successful. Iron levels were easily reduced to less than 0.30 mg/l (EPA recommended level) in all successful pilot plants. Success in manganese removal has been variable during pilot studies, because of the reduced acclimation time and limited recharge volumes used. Complete manganese treatment requires full size treatment zones and up to 20 cycles of recharge to meet EPA levels (0.05 mg/l). Manganese removal meets applicable standards in all permanent plants. This can be seen on Table 2.

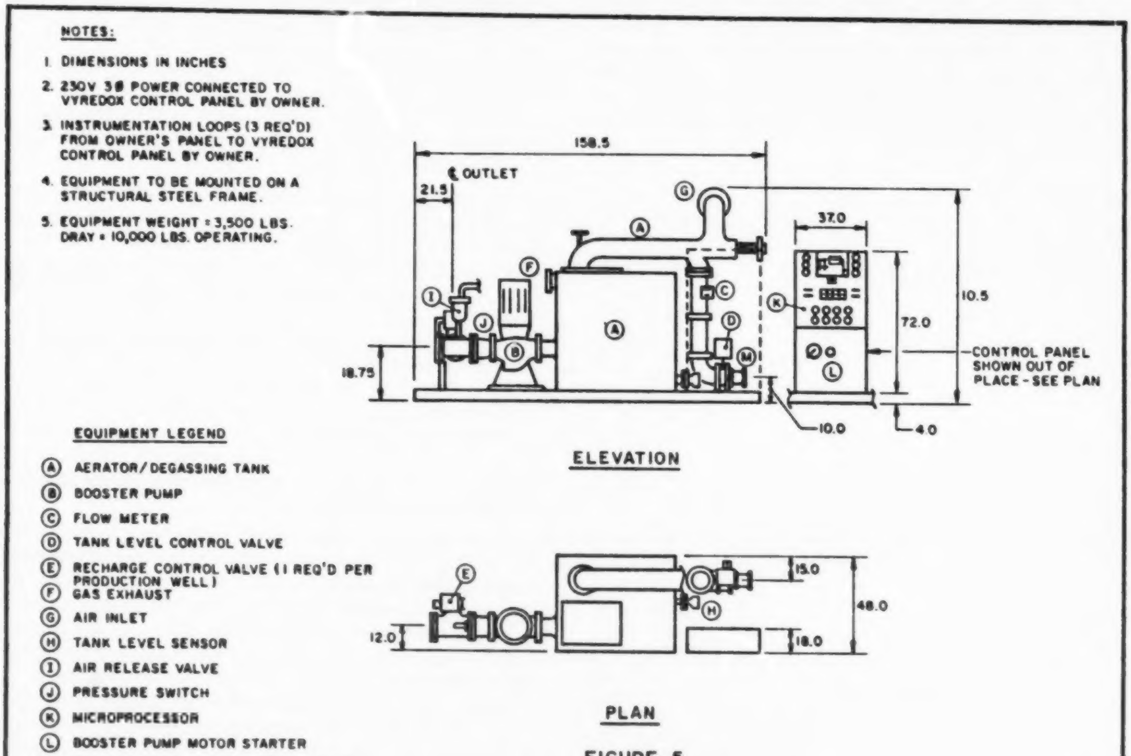
NOTES:
1. DIMENSIONS IN INCHES
2. 230V 3Ø POWER CONNECTED TO VYREDOX CONTROL PANEL BY OWNER.
3. INSTRUMENTATION LOOPS (3 REQ'D) FROM OWNER'S PANEL TO VYREDOX CONTROL PANEL BY OWNER.
4. EQUIPMENT TO BE MOUNTED ON A STRUCTURAL STEEL FRAME.
5. EQUIPMENT WEIGHT = 3,500 LBS. DRAY = 10,000 LBS. OPERATING.
158.5
℄ OUTLET
21.5
37.0
10.5
72.0
CONTROL PANEL SHOWN OUT OF PLACE - SEE PLAN
18.75
10.0
4.0
ELEVATION
EQUIPMENT LEGEND
Ⓐ AERATOR/DEGASSING TANK
Ⓑ BOOSTER PUMP
Ⓒ FLOW METER
Ⓓ TANK LEVEL CONTROL VALVE
Ⓔ RECHARGE CONTROL VALVE (1 REQ'D PER PRODUCTION WELL)
Ⓕ GAS EXHAUST
Ⓖ AIR INLET
Ⓗ TANK LEVEL SENSOR
Ⓘ AIR RELEASE VALVE
Ⓙ PRESSURE SWITCH
Ⓚ MICROPROCESSOR
Ⓛ BOOSTER PUMP MOTOR STARTER
Ⓜ WATER SUPPLY INLET CONTROL VALVE
15.0
48.0
12.0
18.0
PLAN

FIGURE 5
AERATION DEGASSING EQUIPMENT

TABLE 2

VYREDOX PLANT* OPERATING DATA

Town	Country	Date Compl.	Capacity gpm	Water Quality Raw Fe	Raw Mn	Raw pH	Finished Fe	Finished Mn	No. of Wells Production	No. of Wells Recharge	Average Well Depth In Feet	Percentage Of Produced Water Recharged	Percentage Efficiency
Grimsas	Sweden	1971	176	3.9	.07	6.5	0.2	.05	2	12	66	20	80
Holmsjo	"	1971	44	5.2	.16	6.0	0.2	.05	2	6	16	14	86
Stallarholmen	"	1973	220	0.5	.20	7.7	0.2	.05	2	6	46	4	96
Varsas	"	1974	44	1.2	.09	6.1	0.2	.05	2	2	30	11	89
Hovmantorp	"	1976	616	4.0	1.2	6.3	0.2	.05	2	10	18	13	87
Karnsjon	"	1979	660	0.5	.05	6.6	0.2	.05	2	12	80	7	93
Lonsboda	"	1979	308	0.2	.35	5.4	0.2	.05	2	15	26	33	66
Ljungsarp	"	1980	88	0.4	.25	6.3	0.2	.05	1	6	33	33	66
Almesasen	"	1981	307	0.4	.25	6.3	0.2	.05	2	6	59	20	80
Nykoping	"	1981	3608	0.5	.48	8.0	0.2	.05	6	32	118	20	80
Orslevskloster	Denmark	1976	990	1.2	.26	7.6	.05	.02	3	9	200	20	80
Trehoje	"	1977	1320	0.7	.07	7.2	.05	.02	4	12	180	14	86
Stoholm	"	1977	1188	0.6	.08	7.5	.05	.02	3	9	114	14	86
Glyngore	"	1978	1100	0.4	.07	7.7	.05	.02	3	9	225	9	91
Billund	"	1978	990	1.5	.14	7.4	.05	.02	4	12	89	20	80
Karup	"	1980	660	0.4	.07	7.3	.05	.02	2	6	180	25	75
Rodkjaersbro	"	1980	660	1.4	.06	6.9	.05	.02	2	6	160	33	66
Chalon	France	1977	880	0.8	.15	7.1	.20	.05	1	8	33	11	89
Pembroke, MA	USA	1981	400	0.8	.46	5.5	.15	.05	1	8	70	7	93
Seekonk, MA	USA	1983	700	0.3	6.2	7.1	.02	.05	1	6	70	57	43
Endicott, NY	USA	1983	1400	2.7	0.7	7.2	.18	.20	1	3	160	10	90

*Plants listed are those developed by Vyrmetoder AB in Europe and by Hydro Group (formerly Layne-New York Co., Inc.) and Ground Water Associates, Inc., in North America.

Table 2 shows operating data for U.S. plants and plants installed in Europe by Vyrmetoder AB (Vyremetoder AB is the Swedish research firm which developed Vyredox). Vyredox has been applied under a broad range of conditions. Systems with capacities from 44 to 3,608 gallons per minute, iron concentrations from 0.2 to 5.2 milligrams per liter, manganese concentrations from 0.05 to 6.2 milligrams per liter, and pH from 5.4 to 8.0 units have been treated. Well depths have been as shallow as 16 feet and as deep as 225 feet. Finished water is superior to or meets applicable standards in all cases with production water recharged averaging 18.8 percent of water produced.

TABLE 3
NORTH AMERICAN PILOT PLANT DATA
AT FEBRUARY 20, 1984

File No.	No.	Plant Location	Report Date	Well Capacity (GPM)	Raw Water Fe (Mg/l)	Raw Water Mn (Mg/l)	Finished Water Fe (Mg/l)	Finished Water Mn (Mg/l)
1207	1	Wilmington MA	1/78	765	2.70	0.2	0.30	0.10
2785	2	Pembroke MA	12/79	400	0.80	0.5	0.10	0.04
8034	3	Columbus IN	4/81	1,500	1.10	0.3	0.15	0.30
8115	4	Smithville NJ	4/81	700	0.90	0.0	0.60	0.00
8122	5	Ipswich MA	11/81	140	0.16	0.60	0.01	0.05
8129	6	PSE&G NJ	6/82	800	22.0	3.60	0.30	2.00
8130	7	Peabody MA	12/81	1,000	0.58	0.92	0.07	0.10
8133	8	Kirkwood NY	4/82	1,000	3.50	1.30	0.29	0.55
8222	9	Windsor CT	4/82	700	8.80	1.20	0.30	0.96
8223	10	Seekonk MA	4/82	700	2.55	2.30	0.30	2.30
8227	11	Norfolk MA	8/82	150	5.25	0.50	0.21	0
8215	12	Endicott NY	10/82	1,400	2.72	0.71	0.23	0.60
8232	13	Wellesley MA	2/83	TFC 700 WA 700	0.30 0.27	1.0 1.0	0.02 0.03	0.57 0.61
8242	14	Jamaica NY	1/83	700	3.05	0.23	0.37	0.20
8245	15	Middleborough MA	3/83	200	11.25	0.25	0.30	0.23
506	16	Salisbury MA	9/83 10/83	#5 400 TW 40	0.01 2.50	1.40 0.20	0.01 0.30	0.24 0.30
509	17	Mosinee WI	11/83	252	1.60	0.32	0.15	0.28
510	18	Rib Mt. WI	11/83	TW 92	4.00	0.19	0.29	0.12
511	19	Trois Rivieres Ouest, Quebec	2/84	500	4.40	0.18	0.29	0.12
513	20	Valley Stream NY	-	1,000	1.35	0.08	0.29	0.10

SUMMARY

Iron and manganese are common ground water constituents. When present in soluble form they are carried into the water system where, when they settle out, they cause losses in production and transmission capacity as well as consumer complaints about taste and color.

Vyredox removes iron and manganese in the ground before it is pumped to the distribution system, by periodically recharging the ground with aerated water. In-ground removal is the only water treatment method that successfully prevents well screen plugging and capacity loss.

The facilities built for a Vyredox Method plant vary depending on site conditions. Conditions are evaluated before and during construction to custom design each plant for its site environment. Vyredox has proven effective, simple to operate, and economical in removing iron and manganese in a varied range of settings and conditions.

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TRANSPORT PROCESSES

TRANSPORT PROCESSES: SOME THOUGHTS FOR THE FUTURE

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Professor at the University of Strasbourg
Expert Consultant of the Commission of the European Communities

INTRODUCTION

For the specialist of hydrodynamics in porous media, transport processes have become such an obvious part of any groundwater quality study that he finds it very difficult to abandon the rather narrow paths where his research preoccupations have led him and to take a critical global view at the whole domain and at its real place in groundwater quality research.

This specialist has an excuse: the usual approach to water problems has been to divide the hydrologic cycle into various components and to treat them separately and, besides, to consider the basic phenomena pertaining to various disciplines as unrelated. Classically we have surface water studies or groundwater studies; we have chemical research or microbiological research performed without considering transport, or, conversely, transport processes reduced to purely mechanical aspects. Furthermore, applications are also treated separately as illustrated by the classical but maybe not always justified distinction between quantity and quality.

Of course, the complexity of the water system, the lack of data, the lack of fundamental knowledge will justify such an approach, which in many cases is the only realistic way of treating the problems on a short term basis.

The transport of matter by groundwater depends on mechanical, physico-chemical, microbiological phenomena among others, on their interactions and on the conditions on the boundaries of the groundwater system expressing the relationships between groundwater and other components of the hydrologic cycle. A sound evaluation of a transport problem cannot be made without taking into account all its scientific implications in a multidisciplinary approach, which implies that research on transport processes should be conceived as a component of a larger research program on groundwater contamination.

The very complexity of groundwater contamination problems implies long term and expensive research. Thus, the chances that such a research program has of achieving its goals not only depend on its sound scientific construction but also very largely on the financial support it will receive.

Financial support is the concrete expression of the interest raised by a project, which depends sometimes on scientific reasons but usually on various other reasons, for instance economical or environmental, with major political connotation. Past experience has clearly shown that while scientists often know where the scientific difficulties lie, can advise on the kind of experiments that have to be performed and the kind of mathematics that have to be developed, sometimes have intuitive ideas of the results than can be expected and can provide sound guidelines for a research, they have great difficulties in presenting an attractive program as an evocative project relating to groundwater significance in terms of applications to people needs. And of course, as money comes from the people and its management is controlled by people representatives, at least in our democratic societies, we can understand why some good programs, quite justified scientifically, are not accepted.

Not only should transport processes scientists take into account the various scientific disciplines like hydrogeolgoy, microbiology, chemistry and others but also associate themselves to representatives of non-scientific domains, like law, sociology, economy, when preparing their research programs.

As an illustration, take the Environmental Research Programme of the European Community, established for five years (1981-1985) where the research domain covering transport processes explicitly states that it intends to treat all phenomena relating to pollution, from sources to targets in order to obtain the scientific basis necessary for legal measures to be taken as well as standards and criteria to be defined, thus automatically associating transport processes to other disciplines in a politically attractive project.

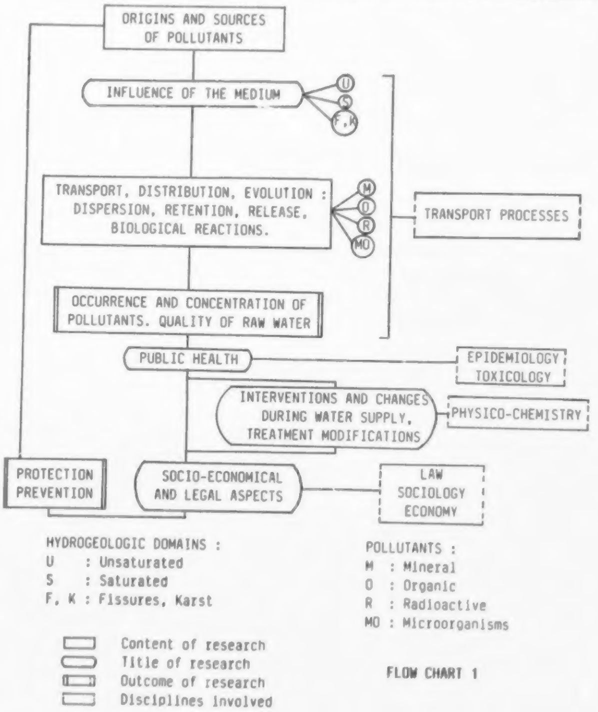
ORGANIZATION OF RESEARCH

My intention in this paper is not to go into the details of possible research programs and present the existing research problems, like for instance the significance of aquifer heterogeneities, the difficulties of measuring them, the difficulties of averaging procedures in the representation of pollutant circulation at various scales, the lack of knowledge we have of the field meaning and values of dispersion coefficients or of the validity of the general diffusion equation to represent dispersion. These research problems are well reviewed in the report "Research for Groundwater Quality Management" by Hall, Piwoni, Pettyjohn, and in my papers, "State of the Art report on mathematical methods of the study of groundwater" and "Groundwater Pollution mathematical modeling: improvement or stagnation?"

I wish to outline broad research ideas, organized around attractive objectives for both those responsible for water resources and scientists.

A research programme has to be organized logically along well defined axes to ensure better presentation to decision makers, better evaluation of financial implications and better follow-up.

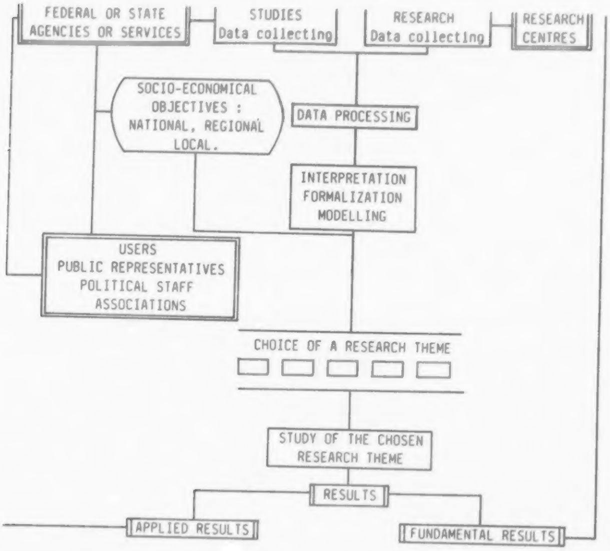
The necessary background on any programme is the hydrologic cycle which provides a spatial axis to organize research, locating in space the various domains where transport processes occur: the unsaturated zone, the saturated zone and the interface between surface and groundwaters. Along the hydrologic cycle, one really follows the path of the pollutants from their sources to their targets. Flow chart 1 illustrates how the hydrologic cycle can be used as the backbone



FLOW CHART 1

of a research programme, displaying the relationships between the various scientific and non-scientific disciplines which interpenetrate the study of transport and showing the importance of a socio-economical objective in the definition of research aims in transport processes.

Organized in space, research has also to be organized in time in order to keep its dynamics and guarantee its impact on the evolving preoccupations of society. Flow chart 2 visualizes a general procedure intended for bringing together the scientists, the agencies which have the responsibility of water resources, and the users themselves, in a concertation to choose the "best" research themes according to socio-economical objectives and the state of knowledge of the phenomena concerned. A time scale can be imposed if necessary on the various themes as well as a timetable for research operations.


FEDERAL OR STATE AGENCIES OR SERVICES
STUDIES Data collecting
RESEARCH Data collecting
RESEARCH CENTRES
SOCIO-ECONOMICAL OBJECTIVES : NATIONAL, REGIONAL LOCAL.
DATA PROCESSING
INTERPRETATION FORMALIZATION MODELLING
USERS PUBLIC REPRESENTATIVES POLITICAL STAFF ASSOCIATIONS
CHOICE OF A RESEARCH THEME
STUDY OF THE CHOSEN RESEARCH THEME
RESULTS
APPLIED RESULTS
FUNDAMENTAL RESULTS

FLOW CHART 2

⬭ Objectives
▣ Participants to research
▭ Content of research
⊏⊐ Outcome of research

SOME THEMES OF RESEARCH

For the coming years, groundwater protection is certainly a major objective. It can be global protection, of the whole aquifer, related to the concept of vulnerability of the aquifer; or it can be local protection, usually of wells or pumping stations, related to the concept of protection zone. From the spatial flow chart, we can introduce four categories of research themes related to groundwater protection in general:

i) exchanges between surface and ground waters:

- river-aquifer exchanges concerning metals or salts;
- aquifer-sea exhcnages concerning metals or salts: the classical salt water intrusion, of course, especially focusing on the miscible transport and dispersion, but also intrusion into the aquifer of chemicals (like metals) released in the sea by polluting industries.
- floods, when they are related to a rise of the water table of unconfined shallow aquifers.

ii) circulation in the insaturated zone:
movements of pollutants with infiltration, dispersion, physico-chemical degradation, adsorption-desorption, mechanical filtering, microbiological effects especially degradation focusing on the estimates of residence times for various categories of pollutants and soils and of survival times of microorganisms, on the study of mobility and persistance of pollutants, on the interactions between the soil, the chemicals and the microorganisms, generally on the so-called purification effects of the unsaturated zone. Metals, nitrates, hydrocarbons, and microorganisms are examples of the most studied pollutants presently; among metals let us cite mercury, lead, chromium. As an illustration of present preoccupations in the European Community, we give in Annex I the lists of pollutants as they have been defined for the legal application of the Community Directive on groundwater protection.

iii) circulation in the saturated zone:
movements of pollutants in anaerobic conditions with convection, dispersion, physico-chemical degradation, adsorption-desorption, mechanical filtering, microbioligical effects expecially degradation focusing on the same themes as in the case of the unsaturated zone, with special attention to heterogeneities of the aquifer, namely preferential paths, and their modeling.

iv) large fissures and karst:
these types of terrains where the classical equivalent continuum assumptions are not valid require specific mechanical and hydrogeological studies and modeling.

These themes are also basically found when studying protection zones. The definition and study of protection zones are important research preoccupations, involving the mechanical, hydrogeological, chemical, physical, biological characteristics of the terrains and of the pollutants in the categories above, and also relationships to legal, economical and political parameters. In that respect, the objective of protecting abstraction points by establishing protection zones is typically a wide interdisciplinary subject where transport processes are the backbone of the study, providing the parameters necessary to estimate the attenuation effects of the physico-chemical and microbiological phenomena involved, principally the residence times, and where science is meaningless without non-scientific considerations of legal, economical and political practice, itself related to land-use problems.

SOME RESEARCH METHODS

Some years ago, research on transport processes used to take place mostly in the laboratory; then, when it was found out that laboratory results could not easily be extrapolated to the field, this being especially true for dispersion, field work became central with the help of mathematical modeling. The taking into account of other processes than purely mechanical, as adsorption for instance and microbiological processes, implies the setting of a methodology where field work and laboratory work are better balanced.

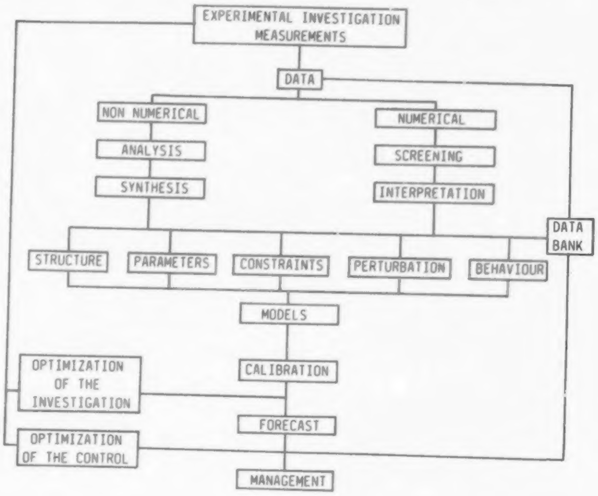
Because of groundwater protection, with respect to health effects, has become a major topic, the microbiology of bacteria and viruses related to their transport in the unsaturated zones is, for instance, a typical subject to be treated in the laboratory on soil columns and then in the field.

More generally, the new development of research, illustrated by the themes quoted in the previous paragraph, focuses on the simultaneous taking into account of phenomena historically classified in distinct disciplines and historically studied with the tools of these disciplines. The realization that these phenomena are not independent, that they overlap and that the resulting effects are not necessarily the sum of the effects resulting from the phenomena considered independent, leads to develop again laboratory work on these interrelationships, adapting the experimental methods. In particular, it seems that computer related soil columns might be an excellent working basis for this interdisciplinary work.

This laboratory work must be connected to field experimentation, which also means that the same research team must be able to take part to laboratory and field work. These two components should appear in any long term research programme.

Last but not least, mathematical modelling is the ever present tool, ensuring systematic processing of the data, helping in their interpretation, providing the link between laboratory and field experimentation, ensuring the necessary generalization of the theories and their applications towards the realization of the objectives of research. Flow chart 3 visualizes the now classical methodology of intervention of mathematical modelling.

Of course, it goes without saying that field and laboratory methods and mathematical modelling are very imperfect tools, the development of which should be part of research preoccupations per se.



FLOW CHART 3

CONCLUSION

Multidisciplinary action, both in the laboratory and in the field, appears to be the backbone of research on transport processes. It implies systematic interpretation of mechanics, physico-chemistry, geochemistry and microbiology, with the setting of integrated experimentation supported by multiphenomena analysis, modeling and interpretation.

It reveals the need to develop multidisciplinary teams which should not be a juxtaposition of specialists but an integration of research people with overlapping knowledges, having a predominant activity in their specialty, of course, but taking some part in all the aspects of the program. As an example, it is important that microbiologists participate in field work on transport and that specialists of fluid mechanics give their advice on microbiological experimentation.

It means that training in multidisciplinary thinking and action should be systematically developed in the postgraduate studies (called in France "education by research") and at professional levels.

Because of the applied character of groundwater studies and the necessity of fulfilling socio-economical objectives, multidisiplinarity should involve non-scientific disciplines and research teams should keep contacts with people working in law, economics, sociology or even integrate them.

Furthermore because of the long term aspect of groundwater quality problems implying rather long studies while the people and hence their representatives do not feel constant concern about water and more generally about the environment, it is necessary to put some effort on explaining problems and solutions to the public, on training it to understand and support research programmes on groundwater.

Eventually, the preparation of research for the future should be coupled to education and training: training or those who will do the research and education of those who finally pay for that research.

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Annex I

LIST I OF FAMILIES AND GROUPS OF SUBSTANCES

List I contains the individual substances which belong to the families and groups of substances enumerated below, with the exception of those which are considered inappropriate to List I on the basis of a low risk of toxicity, persistance and bioaccumulation.

Such substances which with regard to toxicity, persistance and bioaccumulation are appropriate to List II are to be classed in List II.

1. Organahalogen compounds and substances which may form such compounds in the aquatic environment,
2. Organophosphorus compounds,
3. Organotin compounds,
4. Substances which possess carcinogenic mutagenic or teratogenic properties in or via the aquatic environment (1),
5. Mercury and its compounds,
6. Cadmium and its compounds,
7. Mineral oils and hydrocarbons,
8. Cyanides.

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(1) Where certain substances in List II are carcinogenic, mutagenic or teratogenic, they are included in category 4 of this List.

LIST II OF FAMILIES AND GROUPS OF SUBSTANCES

List II contains the individual substances and the categories of substances belonging to the families and groups of substances listed below which could have a harmful effect on groundwater.

1. The following metalloids and metals and their compounds:

   1. Zinc
   2. Copper
   3. Nickel
   4. Chrome
   5. Lead
   6. Selenium
   7. Arsenic
   8. Antimony
   9. Molybdenum
   10. Titanium
   11. Tin
   12. Barium
   13. Beryllium
   14. Boron
   15. Uranium
   16. Vanadium
   17. Cobalt
   18. Thallium
   19. Tellurium
   20. Silver

2. Biocides and their derivatives not appearing in List I.

3. Substances which have a deleterious effect on the taste and/or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption.

4. Toxic or persistent organic compounds of silicon, and substances which may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.

5. Inorganic compounds of phosphorus and elemental phosphorus.

6. Fluorides.

7. Ammonia and Nitrites.

SALINE CONTAMINANTS IN THE GROUNDWATERS OF EASTERN SAUDI ARABIA

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ABSTRACT

Intensive development along a coastline, with consequent rapidly increasing use of local groundwater supplies in the absence of adequate surface resources, invariably leads to intrusion of saline water into the coastal aquifers and the destruction of their water supply potential. Conditions along the Gulf Coast of Saudi Arabia are favorable towards such a chain of events, although for a number of reasons no large-scale intrusion has yet been observed.

This paper reviews the basic intrusion mechanisms, and describes the development patterns as well as the hydrogeologic setting of the Eastern Province. On the basis conclusions are drawn concerning existing, and potential, saline intrusion problems along the Arabian Gulf coast and suggestions are made for corrective and preventive measures to be taken.

INTRODUCTION

It has been well established that the Kingdom of Saudi Arabia is not endowed with an abundance of water resources. Rainfall is sporadic, and evaporation losses are extremely high. Consequently, major emphasis is placed on the rational development of subsurface water resources, a small portion of which occurs as renewable groundwater in shallow formations.

Intensive exploitation of shallow aquifers frequently leads to one or more of the following negative consequences:

- Water tables drop below economic pumping levels,
- Water tables drop below the root zone of vegetation or agricultural crops,
- Lowering of the hydrostatic pressure of the fresh water in coastal aquifers induces direct or indirect seawater intrusion.

This paper deals only with the last-mentioned phenomenon.

The coastline of the Eastern Province extends from Kuwait to Qatar for a distance of about 500 km. The region incorporates the urban conglomerates of Damman/Al Khobar/Dhahran, Qatif and Jubail, while additional development is taking place near Abqaiq and Hofuf, less than 70 km from the coastline. The latter location is particularly significant in terms of water use in view of substantial agricultural production projects, both existing and in the planning phase.

It is evident that current, and projected, development of the coastal region in the Eastern Province of Saudi Arabia makes it possible that problems may arise in the coastal aquifers, caused by intrusion of saline waters from the Arabian Gulf.

Of all the existing groundwater aquifers in the Kingdom, the coastal aquifers constitute a major portion. The most pressing problem associated with coastal groundwater management has been the containment of the gradual increase of salinity, threatening the aquifers' water supply. This increase is attributed to two main factors: First, the chemical diffusion of salty water of the Gulf into the fresh water, secondly, the enhancement of mechanical dispersion as a result of accelerated pumping along the eastern shores of the Kingdom.

Goundwater in the main aquifers usually flows with velocities greater than that of the underlying salt water, because the hydraulic conductivities decrease with depth. In many regions, however, brackish water can be found at shallow depths. This can be attributed to the ever decreasing gradient of the fresh water flow during lengthy dry periods. Combined with excessive pumping this will enhance the upward movement of the underlying salt water zone.

THE HYDROGEOLOGIC SETTING

Groundwater in the kingdom exists in ample quantity, but generally it does not consitute part of the hydrologic cycle and hence ground water "resources" are very limited. In most parts water is trapped in old waterbearing geologic formations with little or no cyclic rates of replenishment. Water in deep aquifers may have been existing since glacial stages, many thousands of years ago (1), and its extraction is comparable to the mining of other non-renewable natural resources.

There are four major formations that constitute the aquifer systems in the Eastern Province which produce economical quantities of water. They are divided according to sedimentary cycles:

1. NEOGENE (Hufuf, Dam, Hardrukh aquifers)
2. EOCENE (Dammam, Rus aquifers)
3. PALEOCENE (Umm er Radhuma aquifer)
4. CRETACEOUS (Wasea, Biyadh aquifers).

The NEOGENE aquifer system overlies the Dammam formation. It consists of isolated patches of unconfined, confined and semiconfined aquifers. There are three clearly divided ithological formations in the system: Hufuf, Dam and Hadrukh. The latter two possess good reservoir properties with the Dam formation being the better of the two. The Hufuf formation is disected by erosion rendering the reservoir quality very poor.

The major recharge of water into this system comes from infiltrated water southwest of the Hufuf region, and from leakage from the underlying Umm er Radhuma aquifer. Other sources of surface recharge are apparent in Wadi Al-Batin and Wadi Al-Sabha.

The gradient pattern of the groundwater flow is from the southwest to the northeast and the slope varies in magnitude from 2.5×10^{-3} southwest of Hufuf to 10^{-4} north of the Ghawar anticline. The system constitutes a major source of water in Hufuf, with withdrawals average 13 m^3/sec. The NEOGENE is a prolific, good aquifer around the Hufuf oasis (400 ppm) with a gradual increase in salinity to 1000 ppm towards the eastern shores.

The EOCENE/Dammam aquifer system underlies the NEOGENE complex. It consists of two aquifers: Alat and Khubar. Although in many areas such a distinction is vague, particularly in the western outcrop, their hydraulic performances differ considerably. The two aquifers have been developed in the populated areas along the Gulf shore. Both formations consist of an upper limestone unit and a lower marl unit. The Alat formation feeds the Ras Tanura and Qatif areas, in some instances it displays erratic productivity due to major variation of hydraulic and storage coefficients. The Al Khubar formation has a more favorable productivity and feeds Dammam, Khubar, and some portions of the Al-Hassa region. The combined thickness of the two aquifers is 0 m in the Ghawar region to 100 m in some other areas. There are more than 1000 wells depleting the system with an average quality of 1000 ppm inland, to more than 6000 ppm along the coast near Abqaiq. The groundwater gradient is in the west-east direction and ranges from 5×10^{-4} inland to 3×10^{-3} northeast of Abqaiq. The seasonal fluctuation is somewhat steady in remote areas, which reflects the possible existence of natural recharge. In the major populated areas, the net annual drawdown, corrected for winter recovery, is 0.3 meters.

The EOCENE/Rus aquifer lies underneath the Dammam formation. Its geological structure is chalky limestone underlain by limestone and dolomite. The Rus formation varies considerably in thickness, thinning out in the area north of the Ghawar anticline (10 meters) and it thickens considerably in the Al-Hassa region. In most cases the Rus formation displays poor aquifer characteristics. However, in some areas, particularly in the Qidam syncline, the formation is valuable as it conveys infiltrated storm water into the underlying Umm Er Radhuma aquifer (M.A.W. 1977).

The Umm er Radhuma (UER) formation lies under the Rus formation and is geologically similar; it is also composed of limestone and dolomite. The structure generally dips uniformly eastward from + 300 meters in the western outcrop to − 200 meters in the Hufuf region. The UER is considered the thickest aquifer (averaging 300 meters) and its upper formation is the most productive for potable water of all aquifers. In most parts, the aquifer is confined by the overlying Rus formation with water table conditions appearing in the west and southwest of the system. In these regions, most of the recharge takes place and flows northeasterly joining existing fossil water towards the confined formations. The eastern zone of this aquifer is less active hydrodynamically due to a noticeable decrease in transmissibility. The quality and quantity of water in this aquifer is suitable for almost any use, particularly in the western part of the structure. Quality, however, deteriorates considerably to the northeast of the aquifer which indicates considerable saltwater intrusion.

The Wasea and Biyadh formations are made up mostly of sandstone and regionally separated by the carbonate SHUAIBA aquitard. The Wasea is a homogeneous deep inland aquifer, becoming somewhat complex in the coastal region. Generally the quality of the water is poor near the eastern shore and it was used for many years for oil extraction in Abqaiq. West of the Ghawar region, the Wasea and Biyadh waters are more potable and they are being used for domestic and industrial purposes in Riyadh.

DEVELOPMENT AND DEMANDS

The largest conglomeration of urban activity in the region is the tri-city area of Dammam, Al-Khobar and Dhahran, where about 500,000 people constitute the population core of the Eastern Province. Activities in Dhahran comprise the headquarters of the ARAMCO Oil Company, the University of Petroleum and Minerals, and major civilian and military utilization of the local airport. Dammam serves as the major trade center for the East coast with large and modern port facilities, a concentration of telecommunication and broadcasting agencies, and excellent road and rail links with the rest of the Kingdom. Al-Khobar provides extensive residential and commercial facilities, while light industry is being established in the inter-urban region.

Within the municipal limits most water is supplied by the Eastern Region Water and Sewage Department, while relies for its domestic services on a mixture of desalinated seawater, and groundwater; the capacity of the current Al Khobar desalination plant is approximately 30,000 m^3/day, which is slated to be expanded by an additional 190,000 m^3/day in 1403 A.H. Local groundwaters are commonly found to be too highly mineralized to be acceptable for drinking purposes, and the blending with desalinated water permits, therefore, complete control over the proper quality of the desired end-product. Water users without access to municipal supplies satisfy their water needs from wells tapping the deep local aquifers. These supplies constitute the non-renewable, fossil water resources of the Kingdom. Their mineral content is usually in the 2000 to 4000 ppm range and hence this groundwater requires some kind of demineralization to bring it up to acceptable standards for potable water (approximately 500 ppm); reverse osmosis equipment is most commonly used for this purpose. For many municipal, industrial or agricultural purposes no treatment is required.

Other significant concentrated areas of water demand include the industrial city of Jubail, which is now under rapid development and is expected to be served, for municipal purposes, by the Jubail desalination unit, which is expected to reach its planned capacity of 250 million gallons/day by 1984, thus making it the largest installation of its kind in the world. About 70 km inland from Dhahran is located the town of Abqaiq, an important staging point for field activities in petroleum exploration and exploitation. Still 50 km further inland, and approximately 75 km from the coastline of the Arabian Gulf, is the Al Hasa oasis, surrounding the ancient city of Al Hofuf; the region is of major agricultural importance and most of the more than 300 MCMY (million cubic meters per year) now being used for agriculture is believed to be utilized for agricultural projects in the Al Hasa area.

A water planning framework for the Eastern region may be adopted from the Third Development Plan (Min. of Planning, 1980) which provides the following "current best estimates" for some parameters constituting a Water Balance in the Eastern Province (all units in MCMY):

		1400	1405	1410	1420
Urban/Industrial uses	(−)	68	153	231	402
Rural/Livestock uses	(−)	1	1	1	1
Irrigated agriculture	(−)	367	470	550	575
Renewable resources	(+)	0	0	0	0
Sub-total (Deficit)	(−)	436	624	782	978

The same source also proposes to cover the deficits with the same mixture of desalination and development of fossil waters as referred to above:

		1400	1405	1410	1420
Non-renewable resources	(+)	1000	1000	1000	1000
Desalination	(+)	11	169	169	169
Reclaimed waste-water	(+)	0	15	25	50
Total (Surplus)	(+)	575	560	412	241

Interesting aspects of this tabulation include the predominant role of water use by the agricultural sector, and the potentially significant contribution to the Water Balance of waste-water reclamation.

In view of the fact that the saline waters of the Gulf not only provide the feed water for desalination projects, but also constitute the source for both direct and indirect intrusion, it is useful to note that the salinity of the Gulf is not uniformly distributed; moreover, its salinity is substantially above that of ocean water (Wojeik and Maadhah, 1981).

CONCLUSIONS AND RECOMMENDATIONS

1. The salinity in all formations below the Eastern Province far exceeds values normally encountered in freshwater aquifers; the source of this salinity is not always clearly identified. Therefore, it is recommended that detailed analyses are conducted, for instance by determining chloride-bicarbonate ratios, of stratified samples from selected deep wells in order to make a definitive diagnosis of the origins of salinity in the region.
2. Even though supplies for municipal purposes in most urban conglomerates appear to be safeguarded in the near future by the construction of major desalination installations, such temporary supplies are likely to be shared among a growing number of local residents (e.g., resulting from new cities such as Al-Jubail), and they are also subject to increasing demands from major distant users (e.g., Riyadh and intermediate localities). Therefore, it is recommended that a systematic management plan be adopted in order to optimize the matching of the quantitative and qualitative potential of each aquifer with the various demands to be reasonably expected to arise from different sectors of the economy in the Eastern Province.
3. It is very probable that the findings of the investigation sub. 1., combined with the management plan sub. 2., will indicate a definite further intrusion problem in the future. Herefore, it is recommended that specific countermeasures be contemplated at the earliest justifiable moment; initial efforts should be directed towards studying the feasibility of using available municipal effluent and existing coastal wells, particularly those already affected by excessive salinities, to build up a coastal pressure ridge and hence to minimize intrusion.

ACKNOWLEDGMENT

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MODELING GROUND WATER TRANSPORT AT CONROE CREOSOTE WASTE SITE

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ABSTRACT

Results from three years of monitoring water quality including organic and inorganic compounds at Conroe, Texas waste site were used to direct simple 1-D and 2-D transport modeling efforts. The U.S. Geological Survey Method of Characteristics Model was used to simulate ground water flow and chloride transport from the Conroe site. Sensitivity analyses were performed on parameters which most affect the plume pattern, including hydraulic conductivity, and the height of the waste pond. "Best fit" combinations of parameters are produced to show the difficulties of matching field data to numerical model results.

Retardation of organics and simple, linear decay due to microbial activity were investigated from available coefficients derived for the Conroe site. Sensitivity of the various coefficients is evaluated in a simple 1-D mode, but such results should be useful in extrapolating such reactions to more realistic 2-D situations.

INTRODUCTION

One- and two-dimensional models were used to assess the potential for migration of contaminants away from an abandoned creosoting facility. The site examined in this project is located in Conroe, Texas, approximately 45 miles north of Houston. Wastes from the creosoting operation were disposed of in three unlined pits from 1952 to 1972. In 1975 the pits were filled in and the land was sold off in three parcels. A housing subdivision was constructed directly over a portion of the pits and down gradient. No water supply wells are known to be down gradient of the plume. Surface soil contamination appears to be the primary hazard. The site has recently been added to the U.S. Environmental Protection Agency superfund list.

The Conroe site is located in the Willis formation of the Chicot aquifer. These deposits are characterized by interbedded sand and clay lenses and overlie a thick, apparently continuous clay basement. The local water table slopes (0.6%) to the southwest towards a small stream. This stream probably alternates as a discharge or recharge to the aquifer depending on rainfall.

The eastern portion of the containment plume has been characterized by the installation and sampling of 14 monitoring wells. Details of this monitoring program are provided elsewhere (Bedient et al., 1984; Wang et al., 1984). No drilling has been done in the subdivision to characterize the western portion of the plume. The major organic contaminants include naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, dibenzofuran and fluorene in concentrations of 100 to 3500 μg/l. Significant increases over background in chloride conductivity have also been observed within the plume. Studies by Wilson et al. (1984) have shown that significant biogegradation of the organics is occuring and is limited by the supply of oxygen.

GROUND WATER TRANSPORT

The transport of contaminants in ground water can be modeled using the solute transport equation:

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} + D \nabla^2 C - W \qquad (1)$$

where D = dispersion coefficient, C = concentration of contaminant, V = average velocity of fluid = Darcy velocity/porosity, x = coordinate parallel to flow, t = time, and W = source/sink term.

The first term on the right hand side of equation 1 represents the advection of the contaminant by the bulk fluid. The second term represents the effects of dispersion or the mixing and spreading of the contaminant front caused by variations in permeability. The source/sink term (W) of equation 1 represents changes in contaminant concentration due to chemical precipitation, adsorption, ion exchange, radioactive and biological decay. These reactions are among the most important since they determine the ultimate fate of the contaminant and are also the least understood. Because of the complexity of these reactions, they are commonly lumped into two terms: (1) "adsorption" where loss of a contaminant is related to the mass of porous media in contact with the contaminant; and (2) "decay" where loss of contaminant is a function of time. The impact of adsorption on contaminant movement is described by the retardation factor, R:

$$R = \frac{V}{V_c} = 1 + \left(\frac{\rho b}{n}\right) Kd \qquad (2)$$

where V = average velocity of the fluid, V_c = effective velocity of the contaminant, pb = aquifer bulk density, n = aquifer porosity, and Kd = partition coefficient. The partition coefficient is a function of the clay content, specific surface area, and soil organic carbon.

Decay, whether biological or radioactive, has generally been modeled as a first order process:

$$C_t = Co\ e^{-kt} \qquad (3)$$

where C_t = concentration at time t; Co = initial concentration; and K = decay coefficient.

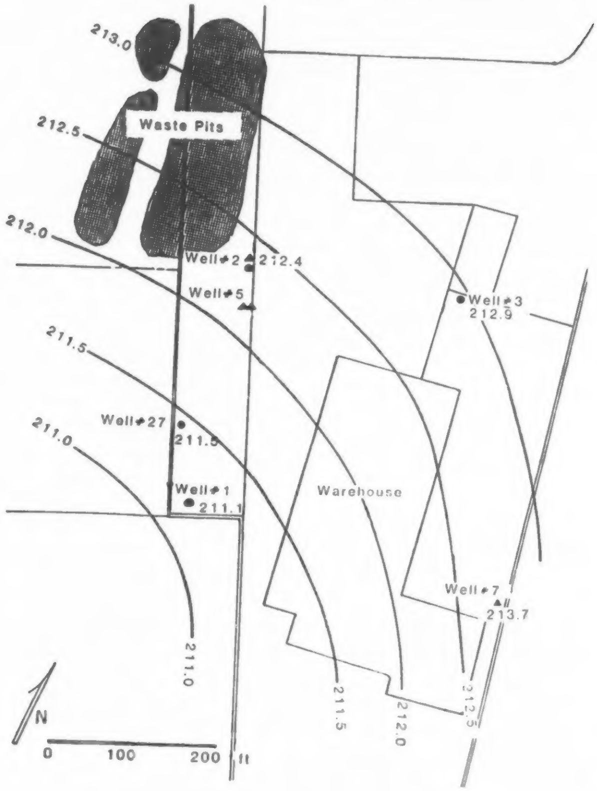
MODELING PROCESS AT CONROE

The modeling process at the Conroe waste site was a two-stage effort. The first stage involved calibration of the 2-D U.S. Geological Survey Solute Transport Model (Konikow and Bredehoeft, 1978) to predict chloride movement. During the second stage, a 1-N analytical model developed by Ogata and Banks (1961) and modified by Bear (1979) was used to evaluate the effects of adsorption and dispersion on organic contaminant migration.

2-D Modeling.

The USGS Solute Transport Model was calibrated to predict water level contours and chloride transport. Figure 1 shows the simulated water level contours and and observed water level elevations. The fit is excellent for all wells except #7. Water levels in well #7 were highly variable, probably indicating a seasonal inflow from the east. This was not felt to be a major control on the larger flow system and consequently was ignored. Figure 2 shows the finite difference grid used for the field site and predicted chloride plume. Constant head nodes were used to drive the system. While the creosoting facility was in operation, seepage from the disposal lagoons probably formed a mound driving the contaminants out into the aquifer. The extent of contamination will be controlled by the leakage rate from the lagoon and the aquifer hydraulic conductivity. Slug tests performed on several wells indicated hydraulic conductivities in the range of 2 to $5\text{x}10^{-4}$ cm/s with an average of $4\text{x}10^{-4}$ cm/s. Since good leakage rate was unknown, this parameter was fit by matching the observed upstream

Figure 1.
Comparison of Predicted Water Table Contours and Well Observations



migration of contaminants. A leakage rate of 2.5 m^3/d resulted in a mound height of 1.2 m and appeared to give the best fit. Predicted and observed chloride concentrations for selected wells are provided in Table 1.

Table 1. Comparison of predicted and observed chloride concentrations.

Well #	Observed Chloride (mg/l)	Predicted Chloride (mg/l)
1	56	51
2	89	87
3	15	18

During the model calibration, it was observed that the extent of contaminant migration was proportional to K and mound height. For a constant injection rate, decreasing K resulted in a substantial increase in mound height, but only a small change in observation well concentrations. This is illustrated in Figure 3 ($K = 1.4 \times 10^{-3}$ cm/s). By increasing injection rate 30% to 3.25 m/d, the predicted chloride concentrations in observation wells 1, 2, and 3 remain essentially identical to those predicted for Figure 2. This is interesting to note since conclusions drawn concerning the plume shape and extent of contaminant migration would be very different for those two simulations. In Figure 2, flow is essentially radial from the ponds and is dominated by the mound, acting as a hydraulic driver. Since the pond has been filled in, this driver has dissipated and transport will be controlled by the natural gradiant. In Figure 3, K is higher and consequently the mound beneath the pond has less impact on transport. In this case the natural gradiant controls transport and flow is strongly to the southwest.

Figure 2.
Chloride Plume with Low Permeability

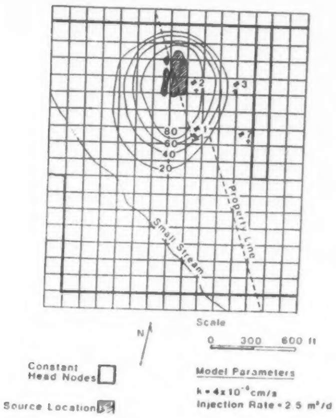
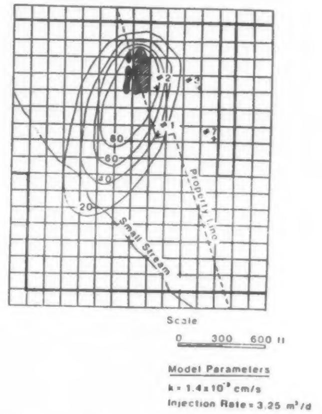


Figure 3.
Chloride Plume with High Permeability



Examination of Figures 2 and 3 illustrates some of the strengths and weaknesses of modeling with a limited data base. The generally radial flow simulated in Figure 2 illustrates that current piezometric gradients may not have controlled transport in the past. At the same time, uncertainty about actual hydraulic conductivity precludes any firm conclusions about the rate of ground water movement. Until wells are placed in the subdivision as part of the 1984 Superfund effort, we can only conclude that the plume will move in a southwesterly direction at a rate of 2.0 to 8.0 m/yr.

1-D Modeling.

A 1-D model was used in this project to assess the impacts of adsorption and biological decay on transport beneath the subdivision. The model selected for use (eq. 4) is a modification (Bear 1979) of the one dimensional analytical solution of the transport equation developed by Ogata and Banks (1961) for a contaminant source undergoing adsorption and decay:

$$C = Co/_2 \; \exp \left\{ \frac{X\,V}{2RD} \right\} \left[1 - Z \right] \operatorname{erfc} \left\{ \frac{RX - VZt}{2\sqrt{DRt}} \right\} \qquad (4)$$

where:

$$Z = \left(1 + \frac{4\lambda DR}{V^2}\right)^{1/2} \qquad 1/\lambda = \text{contaminant half life}$$

Breakthrough with time was studied near the subdivision boundary (60 m). Naphthalene was selected since it is the most common organic at the site and has a comparatively low octanol/water partition coefficient (Log Kow = 3.41). The best estimates of model parameters are shown in Table 2. No single estimate could be made for biodegradation rate since this appears to be oxygen limited. Wilson et al. (1984) observed degradation rates of over 2.5/wk for naphthalene in the laboratory using soil samples collected at the Conroe site. This rate is probably the absolute upper limit for a field situation.

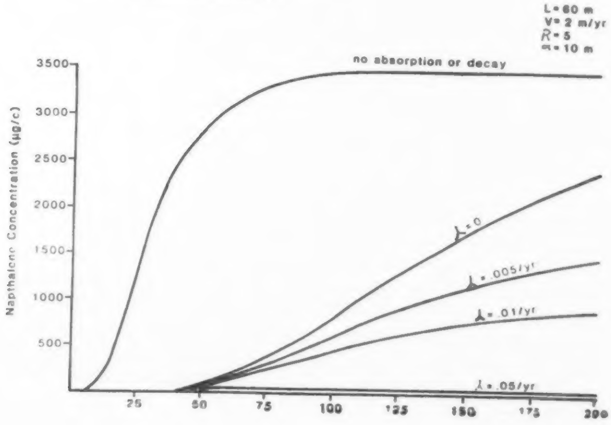
Table 2. 1-D modeling parameters for napthalene transport.

Parameter	Best Estimate
Bulk density	2.09 g/cm^3
Porosity	0.35
Velocity	2.0 m/yr
Dispersivity	10 m
Initial concentration	3500 µg/l
Soil organic carbon	0.04%
Retardation coefficient	5
Biodegradation rate	.001 to 100/yr

The retardation coefficient was estimated using the empirical relation developed by Karickhoff et al. (1979). Soil organic carbon at the Conroe site ranges from 0.01 to 0.04%. At these low organic carbon concentrations the clay content probably is significant in controlling movement of organics and, as such, the calculated retardation coefficients should be conservative.

Figure 4 illustrates the potential effects of biodegradation on naphthalene concentrations at the subdivision boundary A growth rate three orders of magnitude less than those observed in the laboratory would result in essentially complete removal of naphthalene.

Figure 4. Projected Napthalene Concentrations at Subdivision Boundary



CONCLUSIONS AND RECOMMENDATIONS

The chloride plume is moving to the southwest at a rate of 2.0 to 8.0 m/yr. Hydraulic conductivity estimates obtained from slug tests are not accurate enough to more precisely define the rate of chloride movement. Additional monitoring wells should be drilled in the subdivision to the southwest to accurately determine the extent of contaminant migration.

Adsorption and biodegradation can significantly reduce the rate of organic contaminant migration at the Conroe site. Oxygen diffusion into the contaminant plume will control the extent of biodegradation, not the growth kinetics. Future research efforts should be directed towards 1) defining the rates and processes of oxygen exchange and 2) determining microbial growth rates in the field. Once this information has been collected, efforts can then be directed towards modeling the biodegradation process under oxygen limiting conditions.

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GEOHYDROLOGY SURROUNDING A POTENTIAL HIGH LEVEL NUCLEAR WASTE REPOSITORY IN THE PALO DURO BASIN, TEXAS

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ABSTRACT

The Palo Duro Basin of the Texas Panhandle is being investigated as a potential high level nuclear waste repository site. As groundwater is the most likely mechanism for radionuclide movement, it is desirable to locate a repository in a hydrologic regime which is favorable for waste isolation and containment. The Palo Duro Basin consists of deep brine aquifers of low regional permeability underlying a thick Permian age evaporite section. The overlying Permian age evaporites are the Dockum and Ogallala fresh water aquifers.

Observed potentiometric data in the principal aquifers indicate a potential for downward flow from the surficial aquifers to the deep brine aquifers. Groundwater movement in these deep aquifers is very slow. Modeling efforts indicate flow times of hundreds of thousands to over a million years for groundwater to reach the basin margins.

Investigative methods have included drill-stem testing similar to oil field methodology, modified drill-stem testing with tools developed for low-permeability formations and long term production tests similar to conventional water well pumping tests. Testing has generally indicated permeability of .1-10 millidarcies in the water transmitting units.

INTRODUCTION

The Department of Energy's (DOE) National Waste Terminal Storage (NTWS) program is responsible for locating potential sites for disposal of high level nuclear waste. The screening process has identified two potential sites in the Palo Duro Basin of West Texas (Figure 1). Portions of Deaf Smith and Swisher Counties are under study, as are other potential sites in Utah, Mississippi, Louisiana, Nevada and Washington.

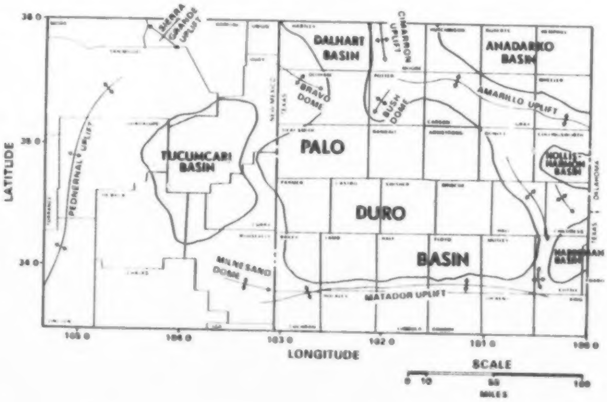
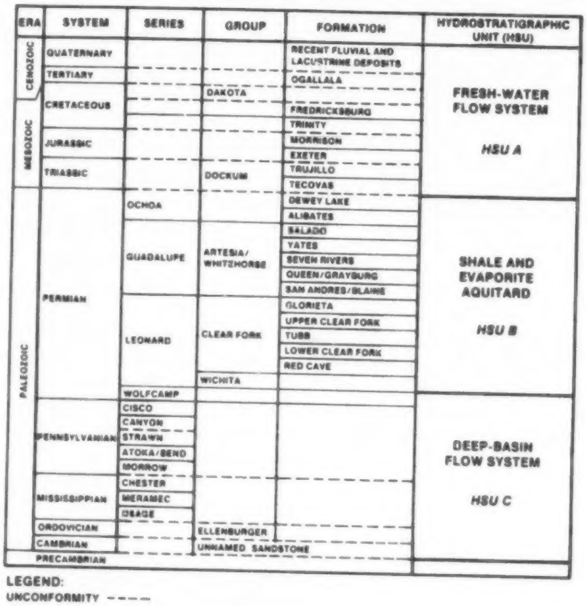


Figure 1. Major Tectonic Features and Major Basins in the Study Area.

Battelle Memorial Institute's (BMI), Office of Nuclear Waste Isolation (ONWI) is responsible for managing the studies of bedded and domal salt sites in Texas, Utah, Mississippi and Louisiana. Stone & Webster Engineering Corporation (SWEC) is Geologic Project Manager for the Permian Basin study. The potential sites in the Palo Duro Basin are two of seven salt sites currently under consideration.

GEOLOGIC AND GEOHYDROLOGIC SETTING

Figure 2 illustrates a generalized stratigraphic column of the Palo Duro Basin in the vicinity of the two potential sites. The geologic formations have been divided into three hydrostratigraphic units. The Upper Hydrostratigraphic Unit (HSU A) consists of the Triassic Dockum Group and the Tertiary Ogallala formation. The Dockum and Ogallala are assumed to be hydrologically connected on a regional scale and are grouped into the same hydrostratigraphic unit. Both are fresh water bearing, although the Dockum becomes saline near its base. The Ogallala is heavily used for irrigation, industrial and municipal water supplies throughout the Texas High Plains.



ERA	SYSTEM	SERIES	GROUP	FORMATION	HYDROSTRATIGRAPHIC UNIT (HSU)
CENOZOIC	QUATERNARY			RECENT FLUVIAL AND LACUSTRINE DEPOSITS	FRESH-WATER FLOW SYSTEM HSU A
	TERTIARY			OGALLALA	
MESOZOIC	CRETACEOUS		DAKOTA		
				FREDRICKSBURG	
				TRINITY	
	JURASSIC			MORRISON	
				EXETER	
	TRIASSIC		DOCKUM	TRUJILLO	
				TECOVAS	
PALEOZOIC	PERMIAN	OCHOA		DEWEY LAKE	SHALE AND EVAPORITE AQUITARD HSU B
				ALIBATES	
		GUADALUPE	ARTESIA/ WHITEHORSE	SALADO	
				YATES	
				SEVEN RIVERS	
				QUEEN/GRAYBURG	
				SAN ANDRES/BLAINE	
		LEONARD	CLEAR FORK	GLORIETA	
				UPPER CLEAR FORK	
				TUBB	
				LOWER CLEAR FORK	
				RED CAVE	
			WICHITA		
		WOLFCAMP			DEEP-BASIN FLOW SYSTEM HSU C
	PENNSYLVANIAN	CISCO			
		CANYON			
		STRAWN			
		ATOKA/BEND			
		MORROW			
	MISSISSIPPIAN	CHESTER			
		MERAMEC			
		OSAGE			
	ORDOVICIAN		ELLENBURGER		
	CAMBRIAN		UNNAMED SANDSTONE		
PRECAMBRIAN					

Figure 2 Generalized Hydrostratigraphic Column for the Palo Duro Basin Area of Texas and New Mexico.

The Ogallala is bounded by the Pecos River on the West, the Canadian River on the North and the eastern caprock escarpment on the East. Recharge to the Ogallala is through precipitation falling on the Southern High Plains. Discharge is via pumpage for water supplies and spring discharge along the eastern rock escarpment. Water use exceeds recharge and water levels are declining in the Ogallala aquifer. Information on HSU A is abundant as the large number of wells provides a broad data base. Data complied by the Texas Department of Water Resources (1982) has been used to construct a water level map of the Ogallala (Figure 3).

The Middle Hydrostratigraphic Unit (HSU B) consists of Permian age evaporites and shales, including the Lower San Andres Unit 4 salt which is the proposed repository horizon. The Middle Unit is considered a regional aquitard.

A relatively small amount of hydrologic data is available for the Middle Unit in the vicinity of the two sites. Core recovery, geophysical logs and drill-stem tests (DSTs) run in DOE-funded exploration

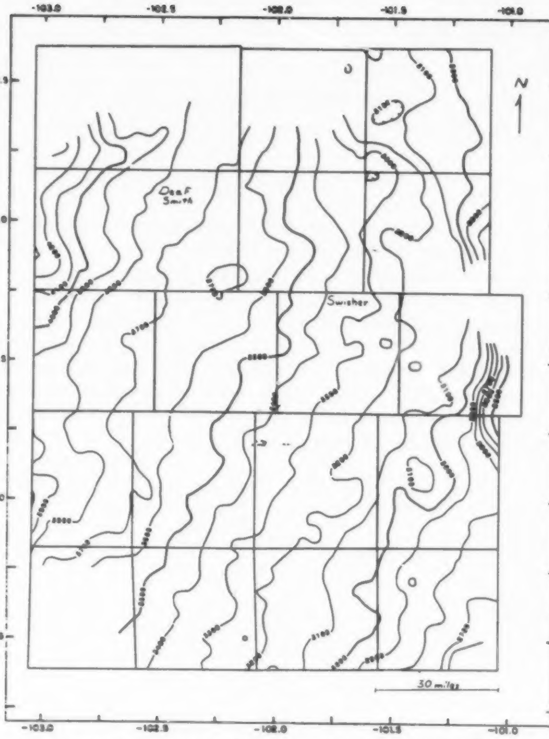


FIGURE 3 RECENT WATER LEVELS FOR STUDY AREA

wells has provided the bulk of available data for these formations. The Cycle 4 Dolomite is considered to be the most permeable unit in the vicinty of the repository horizon and the DSTs indicate permeabilities of less than 0.4 millidarcies (SWEC 1982 and 1983). The existence of bedded salt over geologic time suggests that dissolution rates are quite slow and that the area is relatively stable.

The Lower Hydrostratigraphic Unit (HSU C) consists of Pennsylvanian age "granite wash" arkosic sandstone, Pennsylvanian carbonates and Permian age Wolfcamp carbonates. These deep brine aquifers are separated by various deep basinal shales but may be regionally grouped into one hydrostratigraphic unit.

HSU C has a depositional history consisting of a variety of lateral and vertical facies changes between the shales, carbonates and sandstones. Thick sequences of "granite wash" arkosic sandstones are present along the flanks of crystalline uplifts which bound the basin, the Amarillo uplift to the North, the Bravo Dome to the Northwest, the Pedernal uplift to the West and the Matador uplift to the South. These sandstones gradually thin towards the center of the basin. Recharge to the deep basin aquifers occurs in the outcrop areas in New Mexico and through the permeable arkosic sandstones along the pedernal uplift in New Mexico. Carbonates mark the shelf edge and have migrated with time through the basin. Shales are present in the center of the basin where deep-water conditions existed during deposition. Discharge areas for the deep aquifers are thought to be areas where Pennsylvanian rocks cropout in Oklahoma, east of the study area.

The Lower Unit brine aquifers have been explored for oil and gas production throughout the Palo Duro Basin. Drill-stem tests provide 5502 formation pressure data points in the basin (SWEC 1983). Initial examination of the data indicated that the pressures in the deep aquifers were sub-hydrostatic and that equivalent fresh-water heads (Figure 4) were several hundred to over a thousand feet below heads measured in the overlying Ogallala (Figure 3). This definite downward potential for flow across the salt section to the deep basin brine aquifers resulted in an evaluation of the Lower Unit aquifers.

A classification system was set up to eliminate poor-quality DST data and to index the remaining data. A scheme based on availability of Horner plots and duration of shut-in time was devised to classify the data. About 20% of the data were considered useable following the classification.

These data were used to generate potentiometric surface maps of the deep-basin aquifers. The Wolfcamp potentiometric map is shown as an example (Figure 4). The potentiometric map for the Pennsylvanian aquifer shows similar features. The map shows mounds and depressions which were not expected in this deep system.

A more detailed look at the data revealed producing oil and gas fields around the mounds and depressions. Each data point was then

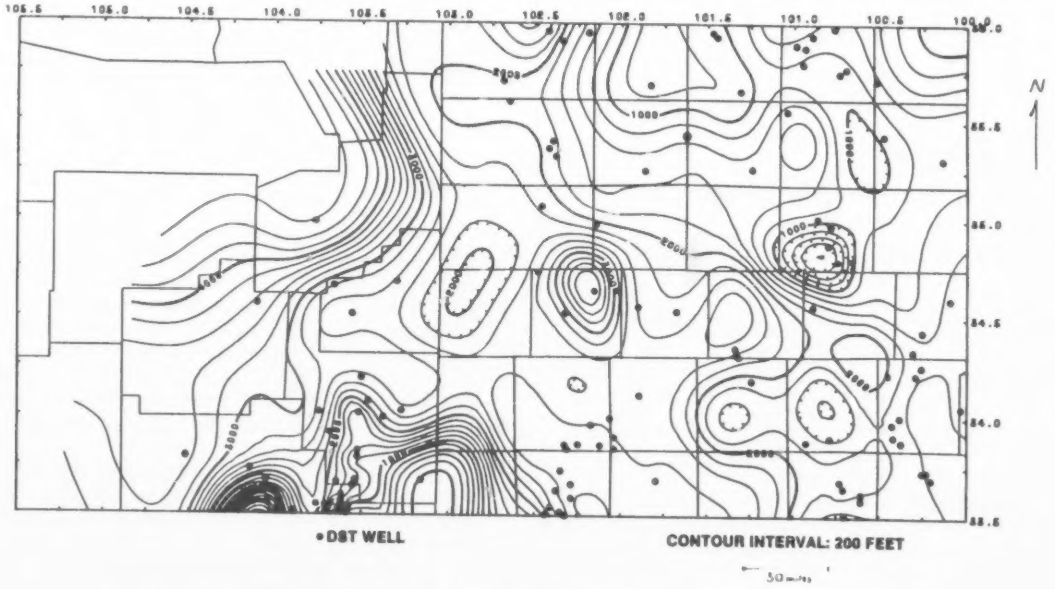


Figure 4 Initial Wolfcamp Potentiometric Surface.

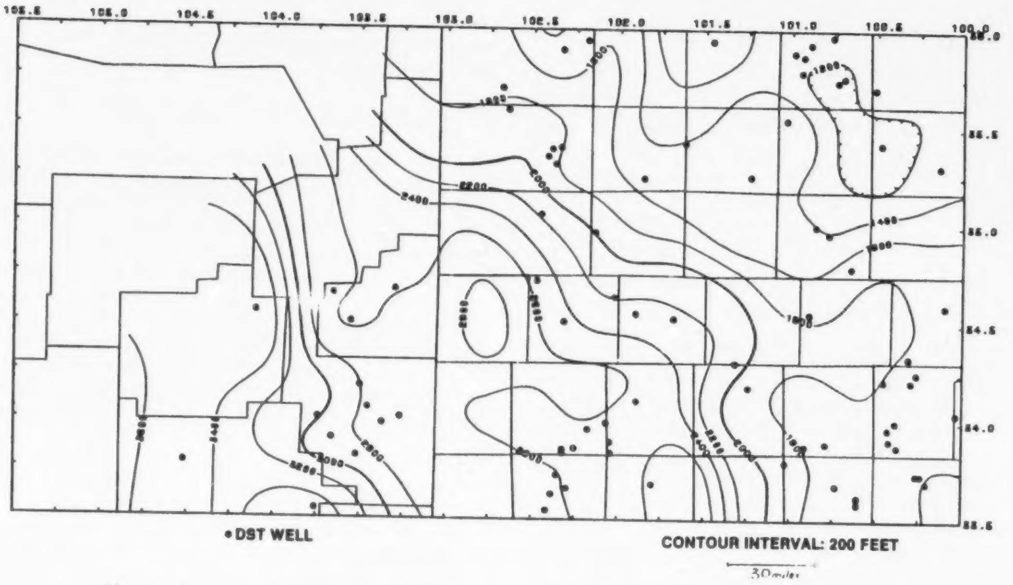


Figure 5 Wolfcamp Potentiometric Surface after Culling Depressured, Underpressured, and Overpressured DST Data.

checked to determine the date the test was run. The data points which were causing the depressions were generally found to correlate with oil-producing zones (SWEC, 1983). These under-pressured data points were removed from the data sets along with several abnormally high pressured points. The high pressure points showed pressure which would correspond to water levels several hundred feet above ground surface and were considered statistically invalid.

A second potentiometric map was produced without the data points which were eliminated (Figure 5). This map provided a much smoother surface and shows a flow direction to the northeast, toward the Amarillo Uplift.

Permeability values are limited for the deep basin aquifers and were derived mainly from tests of suspected oil and gas producing intervals which may have biased the values. Geometric mean values for a limited number of the Wolfcamp and Pennsylvanian carbonates have been determined by the Texas Bureau of Economic Geology (TBEG 1982) and Stone & Webster Engineering Corporation (SWEC). Although the data base is slightly different, the mean values are similar. For the Wolfcamp, TBEG calculated a mean of 1.4 millidarcies (md); SWEC calculated 1.5 md. For the Pennsylvanian, TBEG calculated 3.9 md; SWEC calculated 1.3 md. SWEC has since compiled a data base of 2700 permeabilities for the study area and is in the process of statistically analyzing it for lithic and formation trends. Preliminary results indicate regional permeabiliies of less than 1 md for HSU C.

The potentiometric maps and early permeability data, along with other pertinent geologic data, were used by INTERA Environmental Consultants, Houston, Texas, to develop a regional groundwater model for the Palo Duro Basin. The modeling effort attempted to take the various pieces of data and generate a consistent geohydrologic conceptualization. The intent was to define the flow direction and rate, and to determine the sensitivity and uncertainty in the data base (INTERA 1982).

Many simulations were performed using various values for hydraulic parameters combined with varying boundary conditions. The results of those simulations were compared with observed conditions in an effort to ascertain their validity. Simulations B and F shown on Figure 6 are considered representative of actual conditions in the deep basin flow system. The difference between the two simulations is the assumed horizontal conductivity (Kh) of the "granite wash" sandstone along the Amarillo Uplift. If a high Kh is chosen, the uplift acts as a sink and pulls the flow lines to the northeast toward the uplift and then parallel to the uplift as shown in Simulation F. A Lower Kh along the uplift, Simulation B, has a less pronounced effect but flow is still to the east-northeast from Deaf Smith and Swisher Counties.

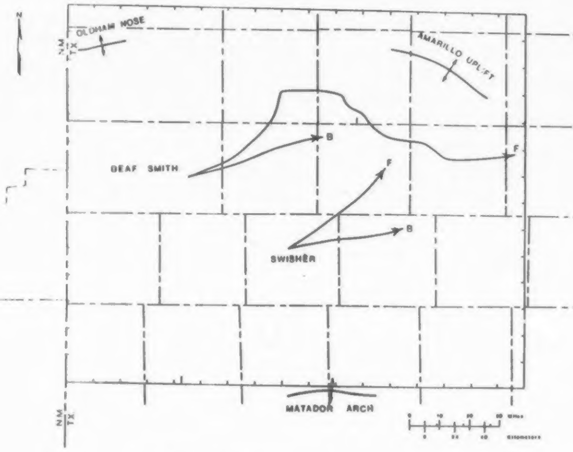


Figure 6 Travel Paths in the Wolfcamp Carbonate: Deaf Smith and Swisher Counties, Simulations B and F.

Travel times were also calculated for both sites. Table 1 lists the time required for a particle to travel 10 KM when introduced into the Wolfcamp or "granite wash" aquifers at reference positions in Deaf Smith and Swisher Counties.

A two-dimensional steady state cross section flow model was constructed by Smith (1983) to model flow perpendicular to the potential lines shown on Figure 4. Flow through each potential repository site was modeled. Wolfcamp travel times of 1.6 million years and 1.4 million years for the Swisher and Deaf Smith sites (respectively) closely resemble those developed independently by INTERA.

Table 1

10 KILOMETER TRAVEL TIMES

Run/Formation	TRAVEL TIME (Years)	
	Deaf Smith Co.	Swisher Co.
B/Wolfcamp	1.1×10^6	1.1×10^6
B/Granite Wash	1.5×10^4	1.2×10^4
F/Wolfcamp	8.8×10^5	1.4×10^6
F/Granite Wash	1.2×10^4	1.4×10^4

Although the travel times are well within DOE and NRC guidelines, there are two important considerations when examining isolation and containment.

1. Travel time of groundwater in the salt horizon and surrounding evaporite units. Calculations of travel time from the repository to the Woflcamp using generic values found in literature for permeability and porosity of salt suggest that radionuclides will require 50,000 to 70,000 years to flow through HSU B before reaching the top of the Wolfcamp aquifer. This factor greatly reduced travel times under natural conditions.
2. No estimates of retardation are considered in any of the calculations. The assumption is made that radionuclides will travel at the same rate as the groundwater. In reality, retardation will slow down radionuclide migration considerably and will add another margin of safety to the long term isolation of nuclear waste.

ONGOING AND PLANNED ACTIVITIES

Additional performance-assessment studies of modeling efforts indicate that the results are most sensitive to permeability values and variations in permeability. Hydrologic data collection efforts will concentrate on permeability variations near the site and along the most likely flow paths, as well as the permeability of the repository salt horizon and adjacent low-permeability interbeds. Regional studies will concentrate on recharge and discharge areas of the deep-basin flow system. The Amarillo Uplift is thought to have a thick sequence of "granite wash" arkosic sandstone which may be acting as a groundwater sink for deep-basin fluids. The suspected dischange area is located East-Southeast of the Amarillo Uplift, in Oklahoma. Studies will focus on defining the lithology in this area.

CONCLUSIONS

The Palo Duro Basin may prove to be an acceptable site for storage of high level nuclear waste from a geohydrologic perspective. The bedded salt and adjacent low-permeability formations of the Middle Unit (HSU B) provide excellent isolation characteristics. Under natural conditions, radionuclides will not escape HSU B in at least the first 50,000 years. The downward flow potential will force any accidental release downward to the deep-basin brine aquifers, where flow velocities are very low. Additional studies of near-field hydrology and effects of heat from the repository will shed more light on the performance of a potential repository. Defining permeability variations near the site, along with refinement of basin geology and lithologic correlation from recharge areas to discharge areas, will be made to fully define the study area.

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ADVECTION AND RETARDATION IN AN EXPERIMENTAL PLUME OF SORBING AND NON-SORBING SOLUTES

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ABSTRACT

Values of the zeroth and first spatial moments of the plumes of four sorbing and one non-sorbing solute have been estimated from a spatially and temporally detailed data set collected during the first 410 days of an ongoing groundwater experiment. While still preliminary, these estimates indicate that chloride is behaving as a tracer, with no loss of mass in solution, and is moving with a mean velocity of 9.5 cm/day along a straight line trajectory parallel to the local hydraulic head gradient. Of the four organic solutes, only carbon tetrachloride is behaving as a linearly-retarded, sorbing solute. The other organics are characterized by decreasing mass in solution and decreasing mean velocity, although they are following the same trajectory as the chloride and carbon tetrachloride plumes. Estimated retardation factors for carbon tetrachloride range from 1.6 to 2.1.

INTRODUCTION

In modeling the transport of organic solutes in groundwater it is commonly assumed that plumes of sorbing solutes are linearly retarded relative to plumes of non-sorbing solutes. In addition, the apparent dispersivities of sorbing and non-sorbing solute plumes are assumed to be the same. This paper explores the validity of the first of these assumptions for trace concentrations of several hydrophobic organic compounds in an unconfined, glaciofluvial sand aquifer. Spatial moment analysis techniques are applied to data from an ongoing field-scale transport experiment to obtain quantitative estimates of solute mass in solution and mean plume velocity for comparison with classic transport modeling theory.

THEORY

Models of the transport of conservative solutes in groundwater often are based on the classic advection-dispersion equation (Bear, 1979):

$$\frac{\partial C}{\partial t} = \underline{\nabla} \cdot \left[\underline{\underline{D}}_r \cdot \underline{\nabla} C - C \underline{V}_r \right] \tag{1}$$

where

C = solute concentration

$\underline{V}_r$ = mean solute velocity vector = $[1/R]\, \underline{V}$;

$\underline{V}$ = mean groundwater velocity vector;

$R = 1 + \frac{\rho_b K_d}{n}$ = retardation factor;

ρ_b = bulk density of porous medium;

n = porosity;

K_d = distribution coefficient;

$\underline{\underline{D}}_r$ = dispersion tensor = $[1/R]\, \underline{\underline{D}}$; and

$\underline{\underline{D}}$ = dispersion tensor of non-sorbing solute.

The most important assumptions underlying this equation are that: 1) solute spreading about the mean motion is diffusive (Fickian); 2) sorption can be modeled by a linear and reversible equilibrium isotherm; and 3) the porosity and retardation factor are spatially uniform. All three of these assumptions may be violated in applying Eqn. (1) to a given field-scale problem (cf., Gelhar and Axness, 1983; Rubin, 1983).

The classic transport model of Eqn. (1) predicts that sorbing solutes will be linearly retarded relative to non-sorbing solutes. In addition, it is straightforwardly shown that the ratio of the total solute mass of a plume (in solution and sorbed) to the mass in solution is equal to the retardation factor, R. Both of these properties are examined below for an experimental plume.

MOMENT ANALYSIS

Spatial moments of concentration distributions provide appropriate means for evaluating the advective and dispersive characteristics of solute plumes. If the ijk^th^ moment of a concentration distribution is defined as:

$$M_{ijk} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x^i y^j z^k \, Cn \, dx dy dz \tag{3}$$

then

M_{000} = mass of solute in solution;

$\mu_x = M_{100}/M_{000}$ = x-coordinate of the center of mass of plume;

$\sigma_{xx} = [M_{200}/M_{000}] - \mu_x^2$ = variance of plume about x_c; and

$\sigma_{xy} = [M_{110}/M_{000}] - \mu_x \mu_y$ = covariance of plume in the xy-plane.

Additional terms for the other coordinate directions are defined analogously.

Under the assumptions leading to Eqn. (1),

$$\frac{dM_{000}}{dt} = 0 \tag{4}$$

$$\frac{d\mu_i}{dt} = V_{r_i} \tag{5}$$

$$\frac{d\sigma_{ij}}{dt} = 2D_{ij} \qquad i,j = x,y,z \tag{6}$$

On the other hand, without invoking these assumptions Eqns. (4) and (5) can be taken as definitions of the mean plume velocity and dispersion tensor, respectively. These definitions are consistent with models of dispersive transport which treat spatially variable hydraulic conductivity as the dominant dispersive mechanism (e.g., Gelhar and Axness, 1983).

EXPERIMENTAL DATA

The data used in this study are taken from those collected during the first 15 months of an ongoing controlled field-scale experiment being conducted by a group of investigators from Stanford University and the University of Waterloo. In August 1982, 11.95 m^3 of a solution containing a known mass of selected compounds were injected as a pulse into an uncontaminated portion of the unconfined, glaciofluvial sand aquifer at Canadian Forces Base Borden in Ontario, Canada. The compounds injected include two non-sorbing tracers and five sorbing, hydrophobic organic compounds with a range of expected mobilities and potentials for biodegradation. Table 1 summarizes the composition of the injection solution.

	Conc.	Mass
TRACERS		
Chloride	892 mg/l	10.7 kg
Bromide	324	3.9
ORGANIC SOLUTES		
Bromoform	32 ug/l	0.39 g
Carbon tetrachloride	31	0.36
Tetrachloroethylene	30	0.36
1,2-Dichlorobenzene	332	3.98
Hexachloroethane	20	0.23

Table 1. Injection Solution Composition

As the plumes of these solutes move under the influence of the natural groundwater gradiant, they are being monitored with a dense network of multilevel sampling devices with horizontal spacings of 1.0-3.0 m and vertical sampling point spacings of 0.2-0.3 m. Figure 1 shows the sampling network as of March 1984. The majority of samples have been taken during a series of 1-3 day sampling sessions, yielding detailed three-dimensional "snapshots" of the plumes. A more complete description of the experimental design and procedures is presented in Mackay et al. (1983).

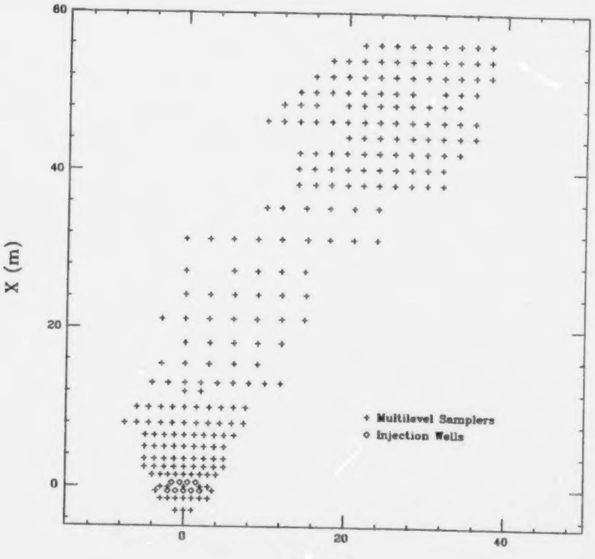

Figure 1. Locations of multilevel samplers and injection wells.

RESULTS

Values of the zeroth and first spatial moments of the experimental plumes of the sorbing and non-sorbing solutes have been estimated from the three-dimensional array of point measurements via interpolation to a regular grid and three-dimensional spatial quadrature. Figures 2 and 3 summarize the results for the zeroth moment, or mass in solution. Figure 2, showing the chloride mass balance, demonstrates that sampling variability is not insignificant and suggests a small positive bias in the estimation technique. The mean of all observations of chloride mass in solution is 11.8 kg with an estimated standard error of estimate of 2.2 kg. This compares reasonably well with the known mass injected of 10.7 kg.

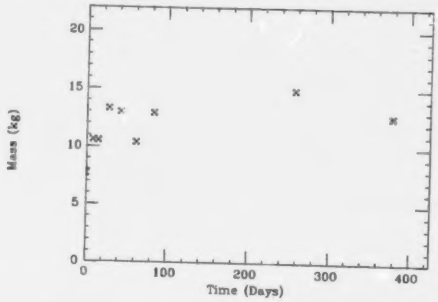

Figure 2. Estimated mass in solution of chloride during first 410 days of experiment.

Figure 3, showing the mass of four of the organics in solution, reveals that only one of the organic compounds, carbon tetrachloride, appears to be behaving conservatively. All of the other organics seem to be undergoing significant decreases in mass in solution over time. Possible explanations for the non-conservative behavior of the other organics include biodegradation, chemical transformation, or irreversible sorption. The average mass of carbon tetrachloride in solution is 0.22 g with an estimated standard error of 0.06 g. Comparing to the estimated total injected mass of 0.36 g, this yields an apparent retardation factor of 1.6.

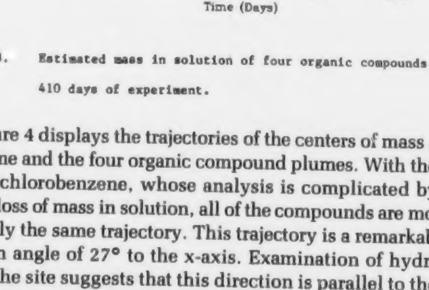

Figure 3. Estimated mass in solution of four organic compounds during first 410 days of experiment.

Figure 4 displays the trajectories of the centers of mass of the chloride plume and the four organic compound plumes. With the exception of 1,2-dichlorobenzene, whose analysis is complicated by its rather extreme loss of mass in solution, all of the compounds are moving along essentially the same trajectory. This trajectory is a remarkably straight line at an angle of 27° to the x-axis. Examination of hydraulic head data for the site suggests that this direction is parallel to the head gradient at the site. While the plumes all appear to be following essentially the same trajectory, they are traveling along that trajectory at different mean velocities. Only the chloride and the carbon tetrachlo-

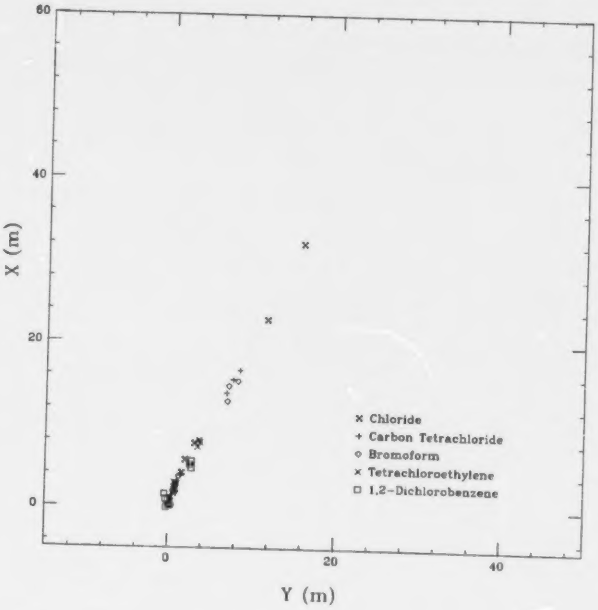

Figure 4. Trajectories of the centers of mass of the tracer and organics plumes.

ride, the two compounds showing no significant loss of mass in solution over time, are traveling at approximately constant velocities. The remaining organics all appear to be decelerating at a rate roughly proportional to their loss of mass in solution.

The estimated mean velocity of the chloride plume is 9.5 cm/day. The estimated mean velocity of the carbon tetrachloride plume is 4.5 cm/day. The ratio of these estimates yields a retardation factor of 2.1, which is somewhat larger than the earlier estimate obtained through use of the zeroth moment. Although this difference may be significant from a practical point of view, it is probably within the estimation error of the moment ratios. In particular, the estimation of total mass of carbon tetrachloride is subject to a large uncertainty.

SUMMARY AND CONCLUSIONS

The preliminary analysis of the lower order moments of a set of experimental solute plumes presented here indicates chloride is behaving as a tracer, conserving mass and moving at a steady and uniform mean velocity of 9.5 cm/day. Carbon tetrachloride is the only organic compound whose average behavior is that of a linearly-retarded, sorbing solute. Estimates of its retardation factor are in the range of 1.6-2.1. The other organic compounds all exhibit behavior suggesting a loss of mass in solution, although their plumes do follow the trajectory of the others. We are currently exploring possible explanations for the observed non-conservative behavior, examining biodegradation, chemical transformation, and soption kinetics and reversibility as potential causes. We are also extending the analysis to second moments in order to examine the dispersive behavior of the plumes.

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CONTRIBUTIONS TO THE FATE OF UNDERGROUND ORGANIC CONTAMINANTS DURING UNDERGROUND PASSAGE

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SUMMARY

For safeguarding drinking water supplies with respect to organic micropollutants information on elimination processes during underground passage is essential. Investigations from natural systems were reviewed. The results do not provide a safe basis for predictions to what extent organic contaminants will be eliminated during underground passage.

A theoretical approach based on phase distributions will more likely allow predictive estimations. However, this asks for reliable data on partition coefficients, especially sorption constants.

Methods of estimating sorption constants so far lead to results with considerable uncertainties. This is demonstrated with experimental data on chlorinated hydrocarbons.

INTRODUCTION

In the Federal Republic of Germany some 70% of the publicly supplied drinking water is groundwater of which only a small percentage undergoes treatment. Another relevant portion is derived from surface water by processes including underground passage (bank filtration, pond infiltration) or migration through sand filters.

To devise protection measures for groundwater catchment areas and to establish dimensions of treatment systems including underground passage or sand filtration for surface waters, in which more and more organic micropollutants are found, a systematic approach to investigate elimination processes in soils and similar systems has become a practical necessity.

Progress in this field was expected from investigations on elimination processes during aquifer passages and from laboratory investigations on mobilities of compounds in soils and geological substrates.

ELIMINATION OF ORGANIC TRACE CONTAMINANTS DURING AQUIFER PASSAGE

To collect data on elimination processes during underground passage a review of investigations on this subject was made. Table 1 represents results from pond infiltrations, well injections, and bank filtration systems, elimination effects are those of underground passage plus eliminations occuring in the boundary zones river sediment or well sediment where considerable biotic activities and contents of soil organic substance may contribute substantially to reduce the contaminations of the water. To a certain extent these processes may be paralleled to those relevant in systems including top soils.

For all compounds evaluated recovery rates were determined by calculating the respective concentration after underground passage in percent of the concentration of the original water (either river or injection water). The resulting picture is very inhomogenous and shows no pattern allowing generalizing conclusions. In every compound class recovery rates between nearly zero and almost 100% occur.

It is concluded that the complexity of the processes in field systems, where dilution and hydrogeological variabilities up to now can hardly be quantified to the necessary extent, does not allow gathering of data for reliable predictions of elimination processes. Only very detailed studies of the respective natural systems could elucidate the specific elimination effects, however, even if all necessary data for this were at hand it still would be tedious.

Tab. 1: Ranked recovery rates of organic compounds after bank filtrations or well injections; summarized from eight investigations (references in MILDE 1981)

compound group	ranked recovery rate (%)	compound
non aromatic hydrocarbons	< 5	octane
	< 60	n-heptane; n-undecane, n-dodecane; undecane*,
	- 100	cyclohexene
aromatic hydrocarbons	< 15	o-xylene; biphenyl; naphtalene
	< 50	toluene; methylnaphthalene (both)
	20 - 100	benzene; m,p-xylene, styrene
highly volatile chlorohydrocarbons	< 5	1,2-dichloropropane
	< 50	carbon tetrachloride
	0 - 75	dichloroethane
	35 - 100	tetrachloroethylene
	50 - 100	chloroform
	60 - 100	1,1,1-trichloroethane, trichloroethylene
further chlorohydrocarbons	< 5	chlorotoluene*; m-chlorotoluene
	< 15	1,3-dichlorobenzene; o-chlorotoluene
	< 35	1,2,3-trichlorobenzene; 1,2,3,4-tetrachlorobenzene, hexachlorobenzene; PCB; pentachlorobutene, hexachlorobutene
	< 75	chlorobenzene; 1,2-dichlorobenzene; trichlorobenzene*, 1,2,3,5-tetrachlorobenzene; dichlorotoluene; tetrachlorobutene; tetrachlorobutadiene; pentachlorobutadiene
	5 - 100	dichlorobenzene*; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; pentachlorobenzene; hexachlorobutadiene
	70 - 100	trichlorotoluene
	- 100	1,3,5-trichlorobenzene; tetrachlorobenzene*
oxygen containing compounds	< 5	toluenylether
	< 40	dichloropropylether; diphenylether
	- 100	dichloroisopropylether
nitrogen containing compounds	< 5	nitrotoluene
	< 40	3,4-dichloroaniline
		N-acetyl-N-ethylaniline
	< 75	aniline; 4-chloroaniline, trifluoromethylaniline
	- 100	2-chloroaniline

* source did not give complete name, possibly identical with compound exactly defined

ESTIMATIONS BASED ON PHYSICO CHEMICAL PARAMETERS

The empirical data presented will not be very helpful for practical purposes, e.g., predicting hazard potentials of handling chemicals in the vicinity of water works wells or assessing underground contaminations. Therefore a different strategy of compiling means to predict elimination processes was followed, in which a rather simple model of the fate of contaminants in the underground was developed. Its main purpose is to estimate potential mobilities which are thought to be determined mainly by phase distributions.

Partition coefficients as a means to predict phase distributions in the underground

All substances attached to the solid phase in soils or geological substrates will be immobile, while dissolved compounds will be transported with the velocity of the respective aqueous phase - in the saturated and insaturated zone. If a gaseous phase is present its content of compounds is subject to translocations governed by concentration gradient (Fick's law). Furthermore only dissolved substances are subject to the major degradation processes in the underground, i.e., by microbes or hydrolysis.

It is therefore evident that even rough estimates of processes in the underground must first of all consider phase distributions. So in the following the validity of predictions methods in this field, as well as the accessibility of necessary data, is focused upon.

Assuming linear distributions between the respective phases the following set of formulas may be derived (Friesel et al. 1984):

$$c_l = K_d \cdot c_s \tag{1}$$

$$c_l = P_{l/g} \cdot c_g \tag{2}$$

$$m_c = c_l \cdot V_t \left[wf + K_d \cdot \rho + P_{g/l} \; (n - wf) \right] \tag{3}$$

c_i = concentration of compound in question in the liquid (l), solid (s) and gaseous (g) phases

m_c = amount of compound in the system,

V_t = volume of the system,

wf = water filled fraction of V_t (V/V_t)

n = porosity (V/V_t)

ρ = bulk density (d. w.)

K_d and $P_{l/g}$ partition coefficients as defined.

In saturated systems, where the gaseous phase may be neglected, (3) becomes

$$m_c = c_l \cdot V_t \; (n + K_d \rho) \tag{4}$$

With these formulas several operations can be performed, e.g., if contaminated water is found in wells, the amount of contaminant in the underground can be estimated and the amount of water necessary to remove the contaminant adsorbed in the aquifer. The geological parameters of the formulas as a rule are accessible either by measurements or by estimate.

Accessiblility and estimation procedures of partition coefficients will be discussed in the following.

Partition between liquid and gaseous phase

Major groundwater contaminations worldwide have been caused by chlorinated hydrocarbons, especially by the solvents tri- and tetrachoroethylene and 1,1,1 - trichloroethane. These solvents are highly volatile and enter groundwaters through the unsaturated zones. So at least for these compounds the relevance of the gas phase in the vadose zone is established.

It has been suggested, that the partition coefficient $P_{l/g}$ of a compound is widely varying concentrations can be calculated by:

$$P_{l/g} = S \; / \; P_v \tag{5}$$

in which S is the solubility and P_v the vapor pressure (both in w/v) of the compound (Kloeppfer et al. 1979). In a lysimeter experiment average $P_{l/g}$ - values were determined for trichloroethene and 1,1,1 - trichloroethane at /µg /l concentration levels (concentrations by Stoettgen 1983). These are compared with laboratory data (Loechner 1981, water/air without soil) and data calculated with equation (5) in Table 2.

Because of uncertainties of solubility and vapor pressure data taken from literature and experimental errors these results should not be overinterpreted concerning the agreement between partition coefficients calculated and measured in the lysimeter experiment. But it can be concluded that the calculation gives a fairly good idea of the phase distribution for these two compounds. They are highly volatile and therefore easy to measure in the gaseous phase. If one considers less volatile chlorinated compounds it is to be kept in mind that quite often their solubilities as well are very low, so in unsaturated systems gas phase concentrations may not be negligible. This is demonstrated for chlorinated benzenes by calculated partition coefficients (Table 3).

Tab. 2.: Liquid - gas - partition coefficients ($P_{l/g}$) from lysimeter experiment (lys.), laboratory (lab.) and calculation (cal.)

compound	$P_{l/g}$		
	lys.	cal.	lab.
trichloroethene	2.31	2.29	2.74
1,1,1-trichloro-ethane	1.63	1.79	0.71

Tab. 3.: Water solubilities (S_w in mg / l) vapour pressures (P_v in Pa), and calculated partition coefficients ($P_{l/g}$) of six chlorinated benzenes

compound	S_w	P_v	$P_{l/g}$
1,2 -dichlorobenzene	145	133	16.6
1,3 -dichlorobenzene	123	228	8.2
1,4 -dichlorobenzene	79	90	13.4
1,2,4-trichlorobenzene	30	38	9.7
1,3,5-trichlorobenzene	19	20	11.8
hexachlorobenzene	$8 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	52.4

The values in Table 3 clearly show that even for substances of very low volatility - e.g., hexachlorobenzene with a vapor pressure of 10^{-8} atm. - the gaseous phase may not be completely negligible. These figures furthermore demonstrate the tendency of HCB and comparable compounds like PCBs towards dispersion in the environment which also can be observed in the underground. Furthermore such considerations may become important for the saturated zone where by evaporation from the groundwater table a concentration gradient may build up with a maximum concentration at the aquifer bottom.

Reinhard (1983, pers. communication) reports a case where in an aquifer contaminated by landfill leachate chloride showed a maximum near the groundwater table, and 1,1,1 - trichloroethane further below in the plume.

Partition between solid and liquid phase

In Germany the most serious groundwater contaminations have been caused by highly persistent compounds. For such substances the primary elimination mechanism in the underground is sorption to the solid phase.

Instead of substrate and compound specific sorption isotherms, for estimation purposes linear partition coefficients (K_d) have been suggested. For a substrate containing more than 0.1% organic matter a K_d value can be calculated from a compound specific K_{oc} value, which is a theoretical partition coefficient between pure soil organic carbon (oc) and aqueous solutions:

$$K_d = K_{oc} \cdot \frac{\% oc}{100} \tag{6}$$

% oc = Organic carbon percentage of substrate

Our investigations with several chlorinated hydrocarbons and different soils showed that this simple approach to sorption allows good estimates for unknown substrates once an experimental K_{oc} is established. Deviations of measured K_d values will not be greater than by a factor of two.

However, the experimental measurement of K_{oc} values for potential groundwater contaminants is expensive and time consuming.

Numerous investigations (Lyman 1982) gave correlations of K_{oc} values of chemicals with other compound properties, which are more easily measured or usually readily available, i.e., the octanol/water partition coefficient (P_{ow}) and the water solubility (S).

Although P_{ow} values probably will be measured for more substances in the future since in the OECD countries they will be required for all new chemicals to be marketed, for the time being these data exist for few compounds only. Furthermore, frequently the P_{ow} is calculated from the respective water solubility of the compound (Kloeppfer et al. 1978).

Since data on water solubility are better available and because the quality of its correlation with K_{oc} does not seem to be less significant than that of P_{ow} (s. Lyman 1982) water solubility is preferred for the estimation of K_{oc}.

For correlations between water solubilities and K_{oc} values several empirical equations have been established (Table 4).

Tab. 4 : Equations correlating K_{oc} and water solubilities of organic compounds (solubilities in mg / l = S_w, in m mol / l = S_p, eq. B and C recalculated with m mol / l)

A	$\log K_{oc} = -0.55 \log S_w + 3.64$	KENAGA a. GORING	1978
B	$\log K_{oc} = -0.54 \log S_p + 3.00$	KARICKHOFF et al	1979
C	$\log K_{oc} = -0.557 \log S_p + 2.606$	CHIOU et al.	1979
D	$\log K_{oc} = -0.686 \log S_w + 4.273$	MEANS et al.	1982

Evaluating our sorption data from different reseach projects with soils and halogenated hydrocarbons (data in Table 5) we calculated the following equations:

$$\log K_{oc} = -0.561 \log S_p + 2.650 \quad r = 0.965$$

$$\log K_{oc} = -0.627 \log S_w + 4.026 \quad r = 0.970.$$

Tab. 5 : K_{oc} values of nine chlorinated hydrocarbons, their water solubilities in m mol / l (S_p) and in mg / l (S_w);

compound	K_{oc}	S_p	S_w
tetrachloroethene	275	0.964	160
trichloroethene	117	8.29	1090
1,1,1-trichloroethane	125	12.73	1700
1,2 -dichlorobenzene	614	0.986	145
1,3 -dichlorobenzene	554	0.837	123
1,4 -dichlorobenzene	498	0.537	79
1,2,4-trichlorobenzene	1670	0.165	30
1,3,5-trichlorobenzene	2090	0.105	19
γ-hexachlorocyclohexane	2550	0.0275	7.6

The resulting equation (with S_p) shows very good agreement with that of Chiou et al. (1982) in Table 4, who investigated a comparable set of chlorinated hydrocarbons. Kenaga and Goring (1978) collected sorption data for a wide variety of compounds, most of them pesticides, Karickhoff et al. (1979) mainly studied polyaromatic hydrocarbons (PAHs), and Means et al. (1982) employed amino - and carboxysubstituted PAHs. Consequently their correlations show considerable differences among each other and with our results. Considering that the equations are logarithmic correlations, deviations for calculated K_{oc} - values may easily exceed one order of magnitude if in a practical problem an equation is used that has been developed for a different set of compounds. At least for the chlorinated hydrocarbons the existing relations allow fairly good rough estimates of phase distributions in the underground. Even for substances with which no experiments with respect to their sorption behaviour have been carried out predictions of their mobilities in the dissolved state are possible. Another application of this is that from an observed distribution of a contaminant in the underground the distribution pattern of similar other substances from the same source may be deduced by comparison of solubilities.

CONCLUSIONS

Evaluation of recovery rates of elimination processes during underground passages in natural systems did not give results useful for prediction purposes. Better results might be attained if the complexity of each system could be accounted for, and processes could be modeled with the necessary resolution. However, this would be tedious and costly.

At present a more promising strategy for prediction purposes seems to lie in the development of concepts for the mechanisms of elimination. For these the main geological and compound parameters can be measured or estimated.

With respect to sorption processes the methods of estimation are at hand, in the future more data should be collected on sorptive behaviour of compounds with differing properties. With these, compound class specific equations to calculate K_{oc} can be developed. They may allow the development of equations more universally applicable by incorporation of further compound parameters beside water solubility; for this purpose theoretical approaches, e.g., the solvophobic theory, may be useful.

At least for the numerous cases of environmental pollution by chlorinated hydrocarbons - solvents, PCB, TCDD - the impact on groundwaters can be assessed with the methods available.

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ASSESSING THE QUALITY OF GROUNDWATER NEAR A COASTAL PLAIN USED FOR AGRICULTURE AND DISCHARGE OF SEWAGE

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ABSTRACT

The quality of groundwater from a new well dug near the coastal plain on Oahu was determined by pumping out 271,500 gallons of water over 1.5 days and analyzing 9 representative samples. No fecal coliforms (< 1/100 ml) and only 1.6 fecal streptococcus/100 ml were recovered in the 9 samples. In addition, no human enteric virus was recovered in the four 100-gallon samples, indicating that the groundwater was not contaminated with sewage. One and three foot soil percolates collected under the ditch which transported sewage near the well were similarly analyzed and the results indicated that it would be most unlikely for sewage-borne bacteria and viruses in the effluent to percolate through the soil profile to contaminate the groundwater. The groundwater was also analyzed for 11 chemicals. The concentration of total dissolved solids (750 mg/l) was the only measurement which exceeded the MCL for drinking water, although the concentration of chloride (241 mg/l) closely approximated its MCL. Blending of this groundwater with high quality groundwater is a viable alternative of increasing the volume of potable water required for urban expansion.

Groundwater is the source of 99% of the drinking water provided to consumers on Oahu, the major island in the state of Hawaii. However, a recent report by the Hawaii Water Resources Regional Study (1979) concluded that virtually all of the existing or planned sources of water on Oahu may be developed to their limits by the year 2000 and therefore plans for future water needs should be implemented as soon as possible. Due to this limited supply of water, plans for urban expansion in some areas have been delayed and developers have been urged to find their own sources of drinking water. A well to provide drinking water was dug by a private developer in southern Oahu. However, several potential problems questioned the suitability of this source of water. First, the well is near a porous coastal plain with high probability of underground seawater intrusion. Second, sewage contaminated water was used to irrigate sugarcane grown extensively in that area. Third, a sewage treatment plant located near the well head was discharging 0.5 MGD of effluent into an unlined ditch.

The purpose of this investigation was to obtain representative groundwater samples by pumping out large volumes of well water and to analyze these samples for indicator bacteria, human enteric viruses and selected chemicals. Moreover, to assess the probability that the practice of discharging sewage effluent into the unlined ditch could result in the contamination of the groundwater with sewage-borne bacteria and viruses.

MATERIALS AND METHODS

Study Site.

The study site is located in southwest Oahu (Figure 1) where the

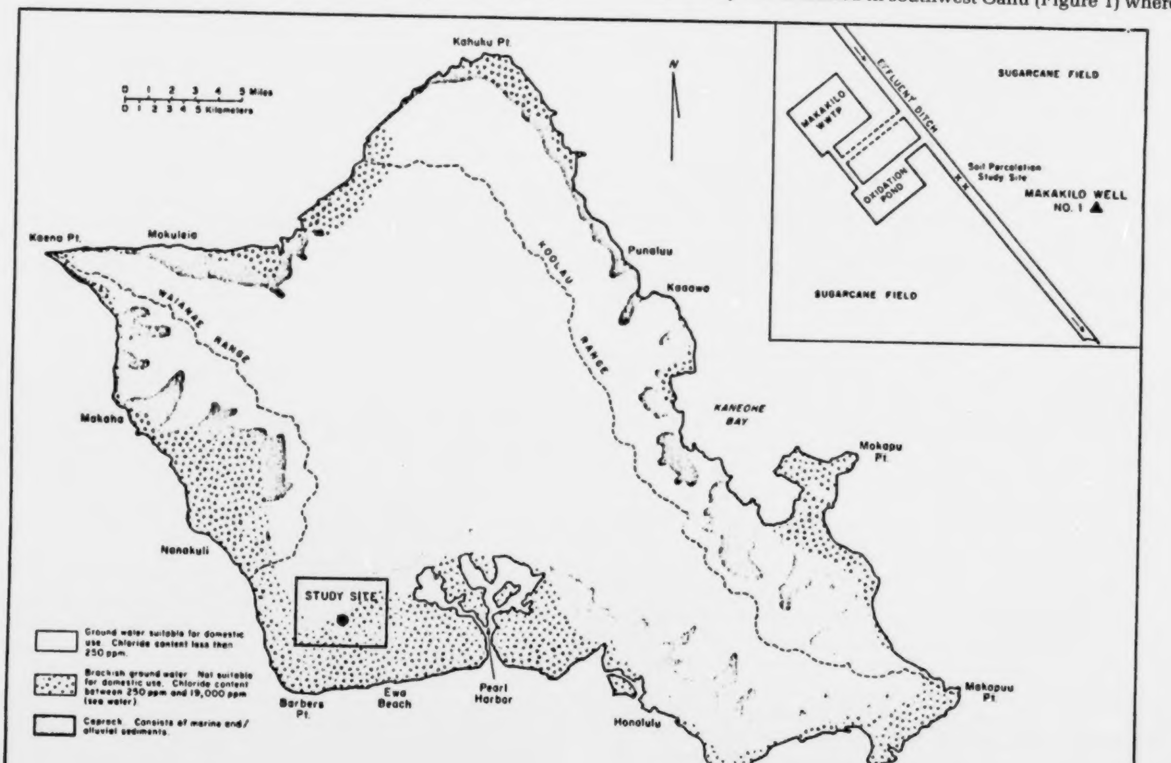

FIGURE 1. Location of study on Oahu and schematic map of sampling sites: Makakilo WWTP, soil percolation, and Makakilo Well No. 1.

Ewa coastal plain, characterized by porous coral rock formations meets the foothills of the Waianae Range, characterized by top soil transported from the mountain. This area has been described as a transitional zone with regard to the geomorphological formation of the island (Ruhe et al., 1965) and has been used primarily to grow sugarcane. Makakilo Well No. 1 was dug in an area previously designated as containing brackish groundwater (Board of Water Supply, 1975). This well is at a ground elevation of 141 feet above sea level and penetrates a permeable, shallow (1-2 feet) top layer of soil characterized as kaolinitic clay plus stable iron and aluminum hydrates (Foote et al., 1972). Below this soil layer lies a zone of 10-20 feet of less permeable, weathered rock (saprolite) followed by permeable and rigid basalt which holds the groundwater. The static water level in the well is 14-15 feet above sea level and the groundwater flows from northeast to southwest along a gradient of 1.3 feet per mile (M & E Pacific, Inc., 1981). The Makakilo Wastewater Treatment Plant (WWTP) is located 0.2 miles northwest of the Makakilo Well (Figure 1) and the effluent from this plant is discharged into an unlined ditch which passes as close as 700 feet west of the well. Although close to the well, the geomorphology of the area of the WWTP differs from that of the well. This area northwest of the well is at an elevation of 160 feet above sea level and is characterized by 5-15 feet of top soil transported from the mountain. This top soil is predominantly silty clay, described as being brown, low humic latasol. Beneath this top soil is 10-20 feet of marine clay described as gray, hydromorphic, montmorillonite followed by saprolite and the basement basalt.

Sampling Design.

The services of a drilling company were contracted to pump out the well at the rate of 400 gpm. To ensure that the samples represented the groundwater source, the pumping of the well was started at 0830 hr on the first day (1-12-82) and was maintained for 8 ½ hr, after which time 178,300 gallons of water were recorded to have been pumped out of the well. The grab method was used to collect 6 water samples at 0900, 1000, 1200, 1400, 1600, and 1700 hr for physical, chemical, and bacteriological analyses. At 1030, 1300 and 1630 hr, water samples of 100 gallons were processed for human enteric viruses. During the second day (1-13-82), an additional 93,200 gallons of water were pumped out over a three-hour period and samples for physical, chemical, and bacteriological analyses were collected at 0915, 1115, and 1200 hr. At 1030 hr, a single 100-gallon sample was processed for virus analysis.

The grab method was used to obtain samples of sewage effluent from the chlorine contact chamber and the oxidation pond located within the grounds of Makakilo WWTP and from the ditch into which the effluent was discharged. To assess the percolative capacities of sewage components through the soil profile, the effluent ditch located 50 yards below the oxidation pond was selected as the study site. The stream at this site was temporarily diverted and the stream bed dug. Two PVC pipes (1.25 inch diameter) were laid at one foot depths while two other pipes were laid at three feet depths. Portions of the sampling pipes were drilled with 8 mm holes and then wrapped with a permeable 12 micron porosity PVC membrane (Porvic, Atlas Minerals & Chemicals Division). One end of the pipe was completely sealed while a tubing was attached to the other end of the pipe. The pipes were covered with the displaced soil and manually packed as well as possible. The effluent was then allowed to flow through this ditch and over these sampling sites. Percolate samples were obtained by applying negative pressure and collected from these tubes twice a week for three weeks to allow the soil to settle before samples collected were actually assayed. The sampling pipes were routinely pumped for 2 hr followed by 1 hr break and a final 1 hr of pumping. By pooling the percolates from the two pipes at each depth, a total of 3-4 gallons of percolate could be obtained from the one-foot sampling pipes while 1-3 gallons of percolate were obtained from the three-foot sampling pipes.

Water Analyses.

Methods as described in *Standard Methods* (1980) were used to measure the chemical and physical parameters of water samples. For the recovery of human enteric viruses, 1-4 gallons of sewage effluent or soil percolates were processed by $AlCl_3$ gel precipitation method whereas 100 gallons of well water were processed by filtration through virus adsorbing filters obtained from Carborundum Co. or Filterite Corp. (Loh et al., 1979). The concentrated samples were inoculated onto cultures of continuous African green monkey kidney cells (BGM), incubated at 36°C for 5-15 days and monitored for multiplication of virus.

RESULTS AND DISCUSSION

Soil Percolation Studies.

To assess the probability that pathogens in the sewage effluent were percolating through the soil profile and contaminating the groundwater, two samples of effluent from Makakilo WWTP and one sample from the ditch were initially analyzed for human enteric viruses. All three samples were positive for virus (Table 1) at concentrations ranging from 1.2 to 16.5 PFU/l. In addition, a chlorine residual of 0.5 mg/l as well as 132 FC/100 ml and 66 FS/100 ml were measured in one of the samples taken from the WWTP. These results indicated that the effluent from Makakilo WWTP was being adequately chlorinated to reduce the concentrations of indicator bacteria but that infectious human enteric viruses were still present in the effluent discharged into the ditch.

Table 1. Analysis of Treated Sewage Effluent from Makakilo WWTP for Infectious Human Enteric Viruses

Date	Source of Treated Effluent	Residual Chlorine (mg/ℓ)	FC	FS	Human Enteric Virus in 4-gal Sample
			--CFU/100 mℓ--		
11-18-81	Chlorine Contact Chamber	0.5	132	66	Positive (1.2 PFU/ℓ)
11-25-81	Chlorine Contact Chamber	Not done	Not done	Not done	Positive (7.3 PFU/ℓ)
12-01-81	Effluent in Ditch	0.2	Not done	Not done	Positive (16.5 PFU/ℓ)

To assess the capacity of sewage-borne components to percolate through the soil, the effluent in the ditch was characterized by 13 selected measurements and the results compared with that of the soil percolates obtained from one and three feet under the ditch. Initially, 4 samples of effluent from the chlorine contact chamber of the WWTP were compared with 2 samples obtained from the oxidation pond. Most of the 13 parameters measured were similar over the four sampling days as well as between the two sources of effluents. However, the effluent from the WWTP was characterized by high residual chlorine (0.8 mg/l) and low concentrations of FC (2 to 64/100 ml) and FS (8 to 66/100 ml). In contrast, the effluent from the ditch was characterized by low residual chlorine (<0.1 mg/l) and high concentrations of FC (5.4 to 120 x 10^3/100 ml) and FS (1.3 to 2.2 x 10^3/100 ml). These results show that the quality of the effluent produced by Makakilo WWTP was consistent and that chlorination was effectively reducing the levels of indicator bacteria. However, in the oxidation pond, chlorine had dissipated, allowing for regrowth of indicator bacteria.

Analysis of 4 samples of effluent obtained from the ditch reflect the source of the effluent. The source of the first two samples was the oxidation pond and these ditch samples were characterized by low residual chlorine (0.2 mg/l) and high concentrations of FC (10 to 190 x 10^3/100 ml) and FS (7.4 to 42 x 10^3/100 ml. The source of the last two ditch samples was the chlorine contact chamber and these two ditch samples were characterized by high residual chlorine (0.7 mg/l) and lower concentrations of FC (60 to 585/100 ml) and FS (730 to 2870/100 ml).

The one-foot and three-foot soil percolates were also analyzed on four separate days. The results in Table 2 show that as the effluent percolates through one then three feet of soil, reduced levels of chlorine, phosphate, silica, TKN, and ammonia nitrogen were observed.

TABLE 2. Water Quality Analysis of Makakilo Effluent and Soil Percolates

Sample Source	Date	Total Chlorine (mg/ℓ)	pH	Conductivity (μmhos/cm)	Total Residue	Ortho-phosphate	Chloride	SiO_2	Nitrogen			FC	FS	Human Enteric Virus per 2-4 gallons
					----(mg/ℓ)----				TKN	NH_3-N	NO_3^-+NO_2^- N	--CFU/100 ml--		
									----(mg/ℓ)----					
Effluent From	12-08-81	—	7.6	1000	576.0	5.5	150	60	—	—	—	2	63	—
Chlorine	12-14-81	—	7.5	1100	601.3	7.5	150	61	29.8	—	0.05	64	66	—
Contact Chamber	12-21-81	0.8	—	1025	540.0	4.9	150	59	22.0	18.4	0.06	32	8	—
	01-27-82	0.8	—	—	528.0	2.6	140	55	14.9	12.8	0.18	63	47	—
Effluent From														
Oxidation	12-08-81	<0.1	7.1	1050	592.0	8.4	100	61	—	—	—	120,000	1,300	—
Pond	12-14-81	<0.1	7.3	1125	590.7	10.0	170	64	29.1	—	0.05	5,400	2,200	—
	12-08-81	0.2	7.1	1000	618.7	9.3	210	61	—	—	—	190,000	42,000	—
Effluent From	12-14-81	0.2	7.5	1100	601.3	10.5	200	64	28.4	—	0.02	10,900	7,400	—
Ditch	12-21-81	0.7	7.5	1000	566.7	5.0	150	60	22.0	18.7	0.07	585	2,870	—
	01-27-82	0.7	—	—	509.3	4.4	150	56	19.0	13.1	0.10	60	730	—
One-Foot	12-08-81	<0.1	7.5	1125	714.7	3.6	150	48	—	—	—	15,800	4,480	Positive
Soil	12-14-81	<0.1	7.4	1400	661.3	4.1	140	47	16.5	—	0.42	308	7,983	Negative
Percolate	12-21-81	0.2	7.3	1200	650.7	2.9	155	47	15.1	13.0	1.08	3,400	1,800	Negative
	01-27-82	<0.1	—	—	448.0	3.4	150	42	11.3	9.2	0.18	43	64	—
Three-Foot	12-08-81	<0.1	7.4	1175	658.7	0.9	160	48	—	—	—	4,630	559	Negative
Soil	12-14-81	<0.1	7.7	1475	849.3	1.1	200	35	14.7	—	0.65	430	500	Positive
Percolate	12-21-81	<0.1	7.5	1575	848.0	0.4	215	33	11.3	8.7	0.26	220	106	Negative
	01-27-82	<0.1	—	—	634.7	1.6	155	32	6.5	5.1	0.11	158	101	—

— = Not assayed.

On the other hand, the levels of chloride and pH remained essentially unchanged while concentrations of conductivity, total residue and nitrate-nitrite in the soil percolates increased. Since these results are similar to an earlier, more extensive study (Lau et al., 1975), we conclude that the packing of the soil over our sampling pipes was adequate and that natural percolation of sewage through the soil was taking place. Analysis of the soil percolates for indicator bacteria reveal considerably fewer FC and FS in the three-foot soil percolates than in the one-foot percolate. Moreover, a pattern of decreasing concentrations of indicator bacteria over 1.5 months was observed in the three-foot soil percolates but was not as apparent in the one-foot soil percolates. These results suggest that with time further packing of the soil occurs and this will reduce the percolative capacity of indicator bacteria. However, more than a foot of soil and closer to three feet of soil is required to consistently retard the movement of bacteria. A similar conclusion can be made with regard to human enteric viruses which were recovered in one of three soil percolates obtained from the one-foot and the three-foot soil depths.

The soil profile in the area of the ditch is characterized by 5-15 feet of silty clay, followed by 10-15 feet of marine clay. These soils contain high concentrations of clay, silica, iron oxide and low pH and humic content. These soil parameters aid in virus adsorption (Lo and Sproul, 1977; Gerba et al., 1981; Sobsey et al., 1980). Finally, in a previous study using a similar type of soil, we (Lau et al., 1975) reported that the maximum percolative depth for polio virus was 46 inches when a sod lysimeter was used, 36 inches when a bare soil lysimeter was used and only 15 inches in an undisturbed soil profile. Based on these cumulative data we conclude that it would be highly unlikely for viable bacteria and viruses present in the Makakilo sewage effluent to percolate through the soil to contaminate the groundwater source.

Well Water Quality.

To directly assess the quality of Makakilo Well water, 271,500 gallons of groundwater were pumped out of the well over 1.5 days and 9 samples analyzed for 11 chemical parameters, indicator bacteria, and human enteric viruses. The chemical characteristics of all 9 samples were similar (Table 3) indicating the homogenous quality of the water drawn from the well. All samples were negative for FC, contained negligible concentrations of FS and all four samples assayed were negative for human enteric viruses. These results indicate that Makakilo Well water was not contaminated with fecal matter.

A composite of the 9 well water samples was also analyzed for dissolved inorganics (36 mg/l Ca, 36 mg/l Mg, 116 mg/l Na, 7.3 mg/l K, 38 mg/l SO_4, 0.08 mg/l PO_4), for total dissolved solids (750 mg/l) and for pH (7.4). The concentrations of all the chemical parameters of Makakilo Well water was substantially higher than that reported for a typical, established potable groundwater source obtained from the base of the Koolau Mountains (see Figure 1) where there is no sewage discharge nor agricultural fields (Visher and Mink, 1964). In this regard, Visher and Mink (1964) concluded that groundwater which receives large volumes of return irrigation water contain increased levels of dissolved solids, chloride, silica, and bicarbonate. These four parameters are especially high in Makakilo Well water indicating that the major source of groundwater for this well is return irrigation water. Despite the elevated concentrations of all parameters measured in Makakilo Well water, only the total dissolved solids of 750 mg/l exceeded the maximum contaminating level (MCL) of 500 mg/l which was established under the secondary drinking water standards. The concentration of chloride (241 mg/l) was the other elevated parameter and approximated its established MCL of 250 mg/l. Thus, blending of this groundwater source with high quality groundwater is a viable

TABLE 3. Water Quality Analysis of Water from Makakilo Well No. 1, Oahu, Hawaii

Sample No.	Hour	Gal. Pumped (x 10^3)	Turb. (NTU)	Total Res. (mg/ℓ)	Spec. Cond. (μmhos/cm)	Cl^-	SiO_2	SO_4	Ortho-PO_4	HCO_3	Nitrogen			FC	FS	Human Enteric Virus/100 gal
						----(mg/ℓ)----					TKN	NH_3-N	NO_3^-+NO_2^- N	CFU/100 ml		
											----(mg/ℓ)----					
12 January 1982																
1	0900	8.4	0.48	582.7	----	240	54	38	0.09	104	<1.0	<1.0	2.5	0	74*	---
2	1000	24.4	0.33	780.0	1075	240	55	34	0.08	108	<1.0	<1.0	2.7	0	55*	Neg.
3	1200	44.3	0.33	806.7	1075	240	55	43	0.09	106	<1.0	<1.0	2.7	0	121*	---
4	1400	33.9	0.38	800.0	1075	230	54	35	0.09	104	<1.0	<1.0	2.6	0	51*	Neg.
5	1600	47.1	0.30	661.3	1075	240	57	35	0.09	106	<1.0	<1.0	2.8	0	5*	---
6	1700	20.2	0.28	789.3	----	240	57	38	0.08	106	<1.0	<1.0	2.6	0	17*	Neg.
13 January 1982																
7	0915	23.2	0.40	709.3	1090	250	55	34	0.08	106	<1.0	<1.0	2.9	0	24*	---
8	1115	37.5	0.25	725.3	1090	240	55	36	0.09	104	<1.0	<1.0	2.9	0	1*	Neg.
9	1200	32.5	0.23	752.0	1100	250	59	37	0.09	106	<1.0	<1.0	2.7	0	1*	---
AVERAGE		30.2	0.33	734.1	1083	241	56	37	0.09	106	<1.0	<1.0	2.7	0	39* (1.6)†	

--- = Not done.

* = Presumptively positive counts; many atypical colonies.

† = Confirmed counts; calculated on confirmation of 4% of presumptive counts.

alternative of increasing the volume of potable water required to serve the needs of southwestern Oahu.

ACKNOWLEDGMENT

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A ONE-DIMENSIONAL MATHEMATICAL MODEL OF VIRUS TRANSPORT

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ABSTRACT

Considerable field work has been performed regarding the fate and transport of viruses within groundwater systems. This paper presents a one-dimensional groundwater flow-mass transport model representing the migration of viruses from a septic system to a private water supply well. Ultimately, the model is designed to determine adequate separation distances between sewage disposal systems and water supply wells.

Inputs to the model consist of separation distance between well and septic system, pumping rate of well, aquifer characteristics, adsorption coefficient for the virus and inactivation coefficient for the virus. The model outputs are relative virus concentrations at various points downstream of the septic system at different times until steady state is reached.

Published values of adsorption coefficients and viral inactivation coefficients for soils and water quality conditions similar to those encountered on Long Island, New York, were utilized as model inputs. From this data and subsequent sensitivity analyses, reasonable conclusions can be drawn regarding the extent of virus transport in the subsurface conditions of Long Island.

This paper primarily focuses on the development of the mathematical representation of the mass transport, adsorption and viral inactivation processes and their natural variability. The sensitivity of the model to these coefficients is discussed and conclusions made as to level of accuracy required in future determination of these factors in the laboratory.

INTRODUCTION

As more and more areas become subject to suburban sprawl, there is an increasingly urgent need to supply potable water and provide for waste disposal in these areas. One of the most efficient and economic means of supplying potable water and waste disposal is the use of on-site water supply wells and septic tank sewage disposal systems. These means of water supply and sewage disposal have been used in rural areas for many years. As an area urbanizes and is subdivided, the practical distances between sewage disposal and drinking water sources decreases to a point where the public health may be jeopardized. Under the influence of suburban sprawl, the question arises as to what is the acceptable distance between these systems before the septic tank system begins to adversely affect the quality of water in the supply well. Of particular concern are viruses which enter the groundwater system through a septic tank system.

Several investigators have shown viruses to be transported horizontally in groundwater from 150 feet to 800 feet under varying aquifer conditions. The methods and economics of groundwater sampling do not lend themselves to an accurate in situ method of determining the maximum transport distance of viruses in groundwater in varying conditions. A more cost-effective method of determining adequate separation distances of sewage discharge is through the use of a calibrated mathematical model of the virus transport phenomenon. The input to this model would be laboratory determined or ranges of coefficients which are much easier to obtain than the field sampling of groundwater.

This paper presents a mathematial model which predicts the movement of viruses from a home septic system to a private water supply well in an unconsolidated geological formation. The input to the model are primarily parameters readily determined in the laboratory for the virus properties and in the field for groundwater flow properties. This is only one type virus transport model which needs development if the viral hazard is going to be completely evaluated. Other possible models would account for large pumpage public water supply wells, flow through fractured rock aquifers, large scale recharge causing groundwater mounding, and the effects of the unsaturated depth to groundwater.

The enteric virus which is the subject of this study is the polio virus. The polio virus has a great deal of sanitary significance, in that it is the cause of poliomyelitis, a disease which in man can be paralytic. Contaminated drinking water is a proven transmission route of poliomyelitis. Although the Salk and Sabin vaccines have all but eradicated the disease in the United States, occasional cases do occur and an increase is expected as fewer and fewer people become vaccinated.

Numerous investigations have been performed that attempt to identify the important factors in the transport of viruses in porous media. It has been found that the transport of viruses is primarily dependent upon four factors:

1. Advection - the average velocity of the water as it passes through the porous media. (Sundaram, 1977; Vilker, 1980; Vilker, in printing).
2. Diffusion - related to advection and is the result of the fact that the actual pore velocities differ from the average velocity and the effect of Brownian motion of the virus particles.
3. Adsorption - the removal of viruses from the groundwater flow through adhesion to soil particles. (Vilker, 1980; Drewry and Eliassen, 1968; Gerba, Wallis and Melnick, 1975; Vilker, in printing).
4. Decay of inactivation - the natural "die-off" of the virus particles due to environmental stresses. (Vilker, in printing; Duboise, Moore, and Sagik, 1976).

The four factors which effect the movement of viruses in a porous medium can be quantified and thereby the concentration of viruses at a point in time and space determined. This can be done by the solution of a form of the mass transport equation for one dimension, as shown (Bear, 1979):

$$\frac{\partial C}{\partial t} = \frac{D}{R_d}\frac{\partial^2 C}{\partial x^2} = \frac{V}{R_d}\frac{\partial C}{\partial x} - \lambda C$$

where: C = virus concentration
t = time
D = coefficient of longitudinal dispersion
R_d = retardation factor due to adsorption following a linear Freundlich isotherm
x = distance from source
V = average velocity of fluid flow
λ = biological decay factor

This is the equation which is solved in the virus transport model.

The radial flow groundwater model used to determine the groundwater velocities in the transport model is a modified version of the model presented by Rushton and Redshaw (1979). This model has been modified to consider only unconfined flow and to use double precision to obtain greater accuracy in determining drawdowns.

DESCRIPTION OF VIRUS TRANSPORT MODEL

The virus transport model numerically solves two differential equations to predict the virus concentrations at a point in time and space. The two equations which are solved are the groundwater flow equation:

$$kh\,\frac{\partial^2 h}{\partial x^2} = n\,\frac{\partial h}{\partial t} + q$$

and the mass transport equation incorporating diffusion, adsorption and decay:

$$\frac{\partial C}{\partial t} + \frac{D}{R_d}\frac{\partial^2 C}{\partial x^2} - \frac{V}{R_d}\frac{\partial C}{\partial x} - \lambda C = 0$$

The output from the drawdown model, groundwater elevations, are then converted to groundwater velocities for input into the mass transport model through Darcy's Law.

The inputs into the virus transport model are the following parameters:

Permeability of aquifer	M^3pd/M^2
Storage coefficient of aquifer	(dimensionless)
Porosity of soil	(dimensionless)
Radius of Well	M
Maximum radius of calculation	M
Location of top of aquifer	M
Location of base of aquifer	M
Location of water level	M
Recharge to aquifer	M
Boundary conditions	1-Constant head boundary 2-Impermeable boundary
Nodes of observation wells	
Pumping rate	M^3/day
Time of cessation of pumping	day
Inactivation factor for viruses	1/day
Longitudinal dispersivity	M
Adsorption factor for viruses	(dimensionless)
Initial virus concentration	pfu/ml
Groundwater gradient	(dimensionless)
Distance from source to well	M

From these parameters, the groundwater flow virus transport model can estimate the virus concentrations at points between the virus source and the pumping well.

To provide realistic output relating to virus transport, the model was run with typical data to represent conditions which may be expected in the Long Island area. The output from this model run at steady state (t equals 57.14 days) is plotted in Figure 1. The most notable result of this model run is the extremely high drop in virus concentration within the first meter of flow, an 80.0 percent removal. Upon reflection, it is seen that a concentration of 1.66 x 10^6 pfu/gal still exists at one meter, far from the recommended standards of 1 pfu/100 gallons or 1 pfu/1000 gallons. The model predicts that virus concentrations on the order of 1 pfu/100 gallons exist between 12 and 13 meters downstream of the source and those on the order of 1 pfu/1000 gallons between 14 and 15 meters. It can be seen from these results that in reality there is little difference in downstream distance between 1 pfu/100 gallons and 1 pfu/1000 gallons. These preliminary unverified results indicate that a 100 foot separation may not be sufficient if either the adsorption factor is greatly reduced or the decay constant is substantially decreased.

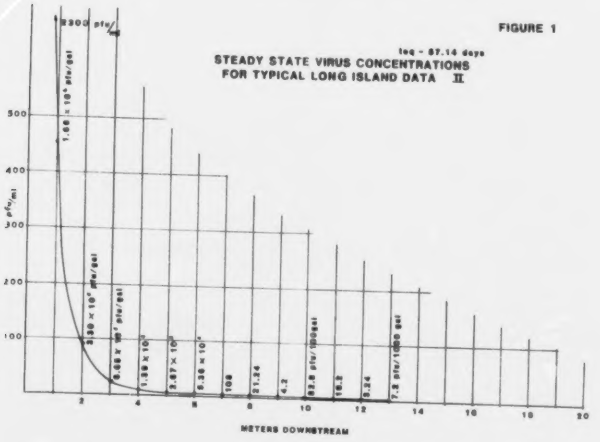


FIGURE 1

STEADY STATE VIRUS CONCENTRATIONS FOR TYPICAL LONG ISLAND DATA II

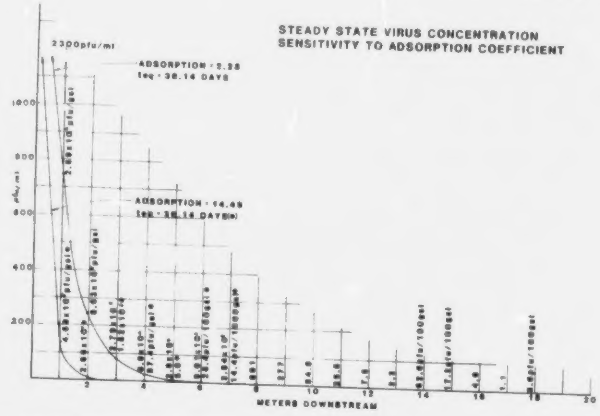
SENSITIVITY ANALYSIS OF VIRUS TRANSPORT MODEL

As a means of obtaining a feel for the response of the model to changes in different coefficients, a sensitivity analysis was performed on the inactivation and adsorption factors. The values chosen for the adsorption coefficients represented the extreme values reported in the literature for sand and gravel. The values of the inactivation coefficient were chosen as the extreme values reported in the literature for slightly polluted and natural waters.

The results of the six model runs, after steady state had been reached, are plotted in Figures 2 through 4. It is evident from the figures that the inactivation coefficient and its range of uncertainty have the greatest impact on the predicted downstream travel of the viruses.

From the results illustrated in Figure 4, it can be seen that the migration of viruses above proposed standards downstream under these hydrologic conditions is beyond 108 feet. This reinforces the speculative conclusion made in the preceding section that a separation distance of 100 feet between cesspool and well is not adequate to prevent viral contamination of the well, under conditions where little adsorption or decay occur.

FIGURE 2



STEADY STATE VIRUS CONCENTRATION SENSITIVITY TO ADSORPTION COEFFICIENT

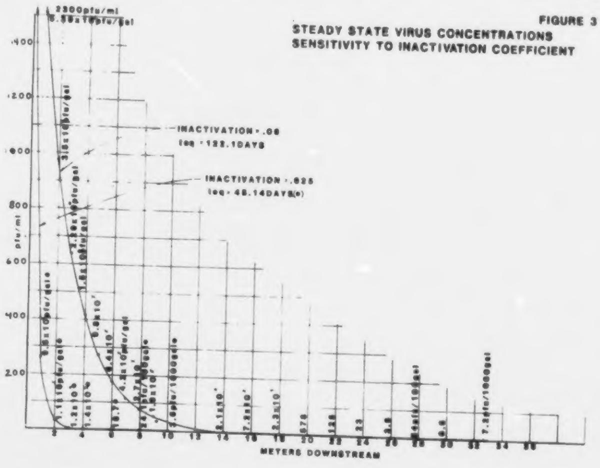


FIGURE 3

STEADY STATE VIRUS CONCENTRATIONS SENSITIVITY TO INACTIVATION COEFFICIENT

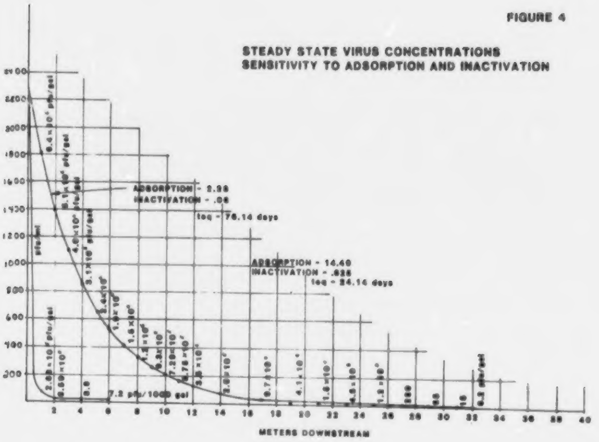


FIGURE 4

STEADY STATE VIRUS CONCENTRATIONS
SENSITIVITY TO ADSORPTION AND INACTIVATION

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APPLICATION OF MULTI-PHASE FLOW THEORY AS A CHEMICAL WASTE LANDFILL, NIAGARA FALLS, NEW YORK

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ABSTRACT

A one-dimensional two-phase fluid flow simulator was developed for Occidental Chemical Corporation to aid design of a remedial action plan for a chemical waste landfill in the Niagara Falls area, New York. A two-phase flow model was necessary because field observations have indicated that immiscible dense organic chemicals exist as a separate fluid phase in the landfill. Under these conditions the effects of capillary pressure forces as well as hydrodynamic and gravitational forces must be considered in order to predict fluid movement and to simulate the effects of various remedial actions.

The two-phase fluid flow simulator was used to identify various hydrogeologic conditions which could be an effective barrier to the downward migration of a heavier-than-water non-aqueous phase liquid (NAPL) from unconsolidated glacial deposits to the underlying bedrock. Analysis of model results indicated that even under a downward hydraulic gradient natural differences in capillary pressure relationships for different lithologies could prevent downward migration of NAPL. It was also determined that in the absence of natural lithologic barriers an upward hydraulic gradient created by an overburden dewatering system could also prevent downward migration of NAPL.

INTRODUCTION

Arthur D. Little, Inc. developed a one-dimensional two-phase flow sumulator to assess the vertical migration potential of immiscible dense organic chemicals. These non-aqueous phase liquids (NAPL) have a specific gravity of approximately 1.55 and consist primarily of tri-, tetra-, and pentachlorobenzene tetrachloroethylene, hexachlorocyclopentadiene, and octachlorocyclopentene (ADL, 1981a). These liquids have been observed in discrete discontinuous zones in the landfill (ADL, 1981b).

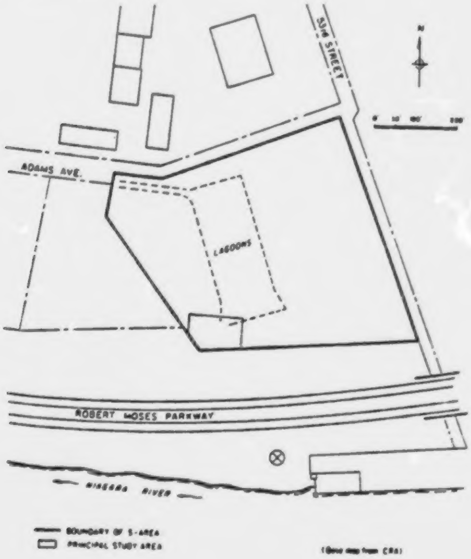

FIGURE 1

S-Area Landfill

This paper describes the application of the simulator to evaluate the effects of capillary pressure differences and upward hydraulic gradients on NAPL migration. Initial applications focused upon hydrogeologic conditions found at the southwest portion of the landfill (Figure 1).

GENERAL DESCRIPTION OF THE SIMULATOR

The numerical simulator developed for these analyses was based on a generalized form of Darcy's law for each of the two fluid phases and general relationships between fluid saturation and capillary pressure. An implicit pressure-explicit saturation method (IMPES) was used in the simulator. The IMPES method combines two single-phase flow equations into a single multi-phase equation based on pressure. The multi-phase equation is solved implicitly for pressure distribution, and the saturation distribution is solved explicitly (Crichlow, 1977).

Input parameters include media and fluid properties as well as saturation dependent functions. These parameters include: intrinsic permeability, porosity, thickness, water phase pressure at model grid endpoints, liquid viscosity and density, relative permeability and capillary pressure functions as well as specification of an initial water and NAPL distribution. Model output consists of water and NAPL saturation at grid nodes as well as nodal water-phase, NAPL-phase and capillary pressure values.

S-AREA HYDROGEOLOGIC SETTING

The hydrogeologic conditions in the S-area landfill have been described in reports prepared by Conestoga-Rovers & Associates Limited (1982) and Leggette, Brashears, and Graham (1980a, 1980b, 1980c). Material contained in these reports was used to prepare Figure 2 which is a summary diagram of conditions in the vicinity of the southwest

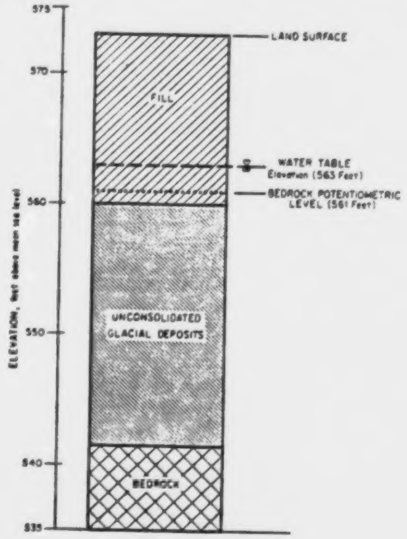
575
570
560
550
540
535
ELEVATION, feet above mean sea level
LAND SURFACE
FILL
WATER TABLE
Elevation (563 Feet)
BEDROCK POTENTIOMETRIC LEVEL (561 Feet)
UNCONSOLIDATED GLACIAL DEPOSITS
BEDROCK

FIGURE 2

Representative Stratigraphic Section of the S-Area Landfill portion of the landfill. Geologic logs indicate a lithologic contact between unconsolidated glacial deposits and bedrock at an elevation of about 541 feet. The base of the unconsolidated glacial deposits is a clay ranging in thickness from about 0.25 feet to almost five feet. The clay is overlain by a relatively thick (16 feet) fine sand layer which contains scattered zones of silt and fine gravel. The fine sand layer is overlain by about 14 feet of artificial fill.

Bedrock water level measurements indicate a potentiometric elevation of about 561 feet. Water levels measured in the overlying unconsolidated deposits indicate a positive head difference between the overburden and the underlying bedrock of between two and 5.5 feet. Under present conditions therefore, a vertical downward flow component exists.

Water transmitting properties of the fine sand and clay have been estimated on the basis of field hydraulic testing (fine sand) done by Leggette, Brashears, and Graham (1980a, 1980b, 1980c) and laboratory permeability testing (clay) done by Woodward-Clyde Consultants. Table 1 summarizes the range of reported vertical hydraulic conductivity values for these two units.

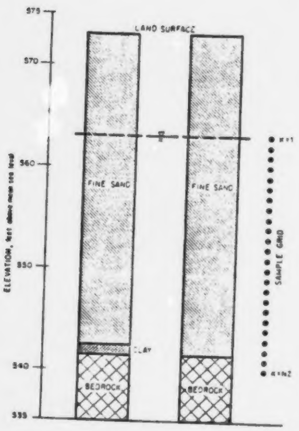

FIGURE 3

Simplified Stratigraphic Sections Used in Model Analyses

Table 1. Reported Vertical Hydraulic Conductivity Values for Fine Sand and Clay at S-Area (from Leggette, Brashears, and Graham, 1980b, 1980c and Woodward-Clyde Laboratory Analysis Report (WCLAR)).

Lithology	Vertical Hydraulic Conductivity (cm/sec)		Source
Fine Sand	0.6×10^{-5}	(0.13 gpd/ft^2)	LBG 1980c
	1.4×10^{-5}	(0.3 gpd/ft^2)	LBG 1980b
Clay	$0.4 - 1.0 \times 10^{-7}$		LBG 1980c
	$2 - 9 \times 10^{-7}$		LBG 1980b
Fine Sandy Silty Clay (Test Hole B-15)	7.9×10^{-7}		WCLAR
Silty Clay (Test Hole B-18)	5.9×10^{-7}		WCLAR
Medium to Fine Sandy Silty Clay (Test Holes B-13 and B-17)	2.7×10^{-5} 1.9×10^{-7}		WCLAR
Clay (Test Holes OW6S-80, OW7S-80)	4.1×10^{-8} 9.8×10^{-8}		WCLAR

MODEL APPLICATION TO S-AREA

The stratigraphic section observed in the southwest corner of the landfill was simplified into three units of fine sand, clay and bedrock, and two basic sections were used in model analyses. The first section included a thin (1 foot thick) clay layer between bedrock and the overlying fine sand. The second section had fine sand in contact with bedrock (no clay layer). Figure 3 illustrates the two principal stratigraphic sections that were used in the analyses.

A. Effects of Capillary Pressure Differences

To evaluate the effect of capillary pressure differences related to lithology changes a series of simulations were made using a three-layer stratigraphic column (see Figure 3). The three layers represented fine sand overlying a one foot thick clay overlying bedrock. The model was constructed assuming a two-foot negative head difference (downward flow) between the water table and bedrock potentiometric level. The vertical hydraulic conductivity of the bedrock was assumed to be 10^{-3} cm/s, for the fine sand it was assumed to be 10^{-5} cm/s and the vertical hydraulic conductivity of the clay was varied from 10^{-5} cm/s to 10^{-9} cm/s. The capillary pressure and relative permeability functions used in the simulations are shown in Figures 4 and 5. The residual saturation values for water and NAPL were assumed to be 20 and 10 percent, respectively.

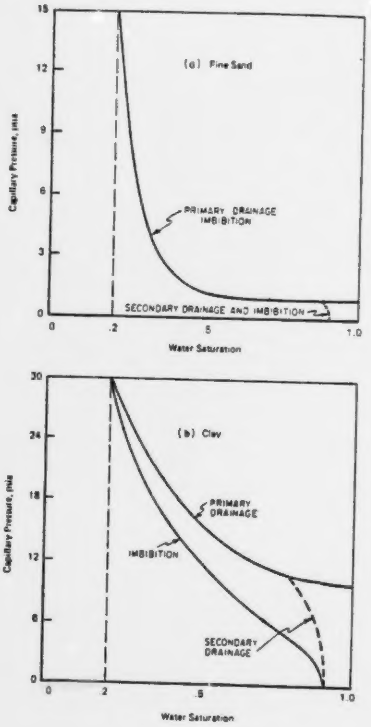

FIGURE 4

Capillary Pressure Versus Water Saturation Curves Used in S-Area Analyses

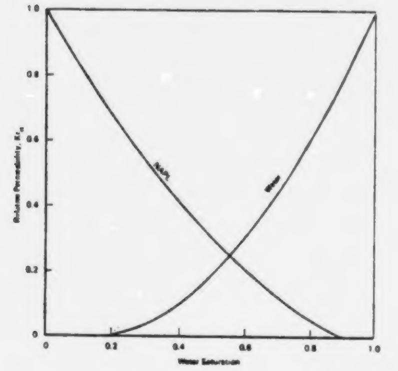

FIGURE 5

Relative Permeability Versus Degree of Saturation

The results of one of the simulations is shown in Figure 6. This illustration shows that NAPL migrated downward through the fine sand, but did not penetrate into the underlying clay layer. This condition was also observed in the other simulations. The analyses verify that differences in capillary pressure relationships can be an effective barrier to NAPL migration from overlying coarser grained materials into finer grained underlying materials (ADL, 1982).

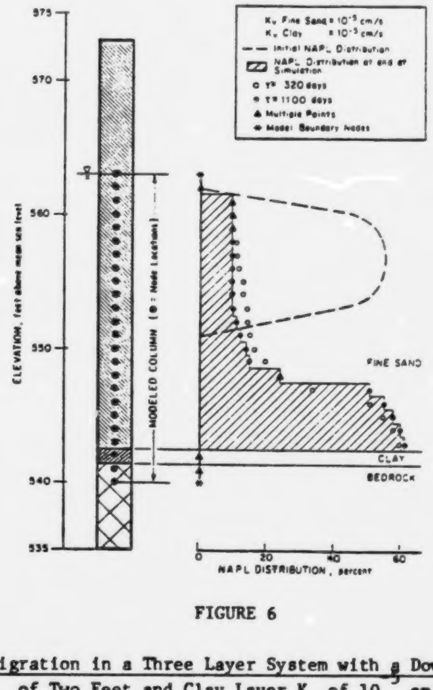

FIGURE 6

NAPL Migration in a Three Layer System with a Downward Head of Two Feet and Clay Layer K_v of 10^{-5} cm/s

B. Effects of Water-Phase Hydraulic Gradient on NAPL Migration

The variation in thickness of the clay layer in the southwest corner of the landfill suggests that there may be areas where the clay has been eroded or was never deposited and that fine sand may be in direct contact with bedrock. Under these conditions the capillary pressure differences described in the previous section may not exist and NAPL migration would be affected primarily by the hydrodynamic gradient.

Implementation of the remedial action plan will cause the water table to be lowered in response to pumping from a drain system. The water-table lowering will create an upward acting hydraulic gradient between the unconsolidated materials and the underlying bedrock. The magnitude of the head difference between the water table and the bedrock potentiometric level will depend on the amount of water-table lowering.

Several simulations were made to evaluate the amount of water table lowering that would create a sufficient upward gradient to prevent downward migration of NAPL. The model analyses were based on a two-layer stratigraphic column (see Figure 3) with a fine sand material overlying bedrock. The vertical hydraulic conductivity of bedrock and overlying material was assumed to be 10^{-3} cm/s and 10^{-5} cm/s, respectively. The bedrock potentiometric level elevation was assumed to be 561 feet and the water table elevation was varied from 551 to 556 feet. Capillary pressure functions for the bedrock and unconsolidated materials were assumed to be identical and equal to that shown for fine sand in Figure 4.

Figure 7 illustrates the effect of lowering the water table from an elevation of 563 feet to an elevation of 552 feet. This figure shows that

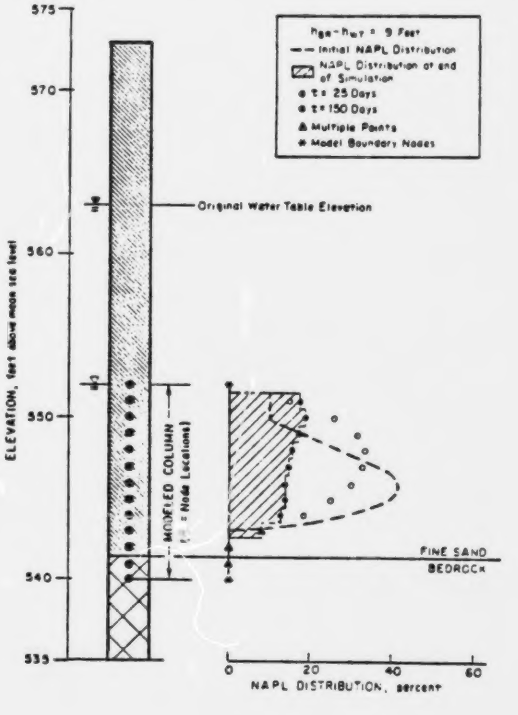

FIGURE 7

NAPL Migration in a Two-Layer System With an Upward Head Difference of 9 Feet within 25 days there would be a noticeable upward movement of NAPL indicating that the nine foot upward head difference was sufficient to reverse the downward migration of the NAPL column.

The results of this series of simulations indicated that implementation of a remedial action plan that creates a minimum upward head difference of nine feet between the water table elevation and bedrock potentiomentric level in the vicinity of a clay layer discontinuity could be sufficient to prevent downward migration of NAPL from the unconsolidated glacial deposits to the bedrock. The length of the NAPL column and the degree of NAPL saturation used in our analysis was greater than has been observed in field investigations at S-area and represent worst-case conditions.

SUMMARY

A one-dimensional two-phase fluid flow simulator was developed and applied to conditions believed to be representative of the S-Area landfill. The simulator was used to identify hydrogeologic conditions which can be effective in preventing downward migration of dense non-aqueous phase liquids (NAPL) consisting primarily of tri-, tetra-, and pentachlorobenzene, tetrachloroethylene, hexachlorocyclopentadiene and octachlorocyclopentene.

Simulations were made to evaluate the effectiveness of lithology dependent capillary pressure functions and various upward hydraulic gradients on downward migration of NAPL. In particular, simulations were made to identify parameter combinations which could create an effective barrier to NAPL migration into the underlying bedrock.

ACKNOWLEDGMENT

The work on which this study is based was funded by Occidental Chemical Corporation. Technical support and critical review of this study were provided by Mr. Jay Cull (Occidental Chemical Corporation), Mr. Francis A. Rogers (Conestoga-Rovers and Associates) as well as Dr. Charles Hadlock and Dr. Philip Levins (deceased) of Arthur D. Little, Inc. The author is particularly indebted to Dr. Levins for his personal interest and contributions to the success of this project.

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MODELLING OF NITROGEN REMOVAL IN THE VADOSE ZONE

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ABSTRACT

Ammonium in secondary wastewater is removed in the vadose zone when wastewater is applied to spreading basins with alternate flooding and drying. The processes involved in the removal of ammonium nitrogen are adsorption of ammonium by the soil, oxidation of the adsorbed ammonium to nitrate by nitrifying bacteria in the subsequent drying period thus freeing adsorption sites in the soil for further ammonium adsorption, and reduction of nitrate to nitrogen gas by denitrifying bacteria during flooding.

The extent of nitrogen removal is governed by the rate of infiltration, the lengths of the flooding and drying periods, the adsorption capacity of the soil for ammonium and the rates of nitrification and denitrification. A model incorporating these processes has been developed, which can be used to explain why nitrogen removal does not take place in some wastewater rapid-infiltration systems, why nitrogen conversion stops after the nitrification state in some cases, and to calculate the extent of nitrogen removal as a function of soil type and operating conditions. The model shows that the approach to steady state after a change in operating conditions is reached only slowly.

The model parameters have been obtained experimentally under laboratory conditions. A case study of nitrogen removal from wastewater by rapid infiltration in Perth, Western Australia is discussed.

INTRODUCTION

Nitrogen removal by land treatment using the rapid infiltration system has been demonstrated in many existing field systems (e.g. Leach et al., 1980). Maximization of nitrogen removal has also been attempted at the Flushing Meadows project (Bouwer et al., 1980), where nitrogen removal from 30 to 65% was achieved, and even higher removal rates were obtained in column experiments when the average infiltration rate was reduced (Lance et al., 1976). The design for rapid infiltration system has incorporated some of the above findings, though it has been realized that nitrogen removal is dependent on soil type and operating conditions (USEPA 1981). The difficulty in translating our understanding of the nitrogen removal processes into design stems from the many variables that are involved, their complex relationships and especially the opposing effects these variables have on nitrogen removal.

In Perth, Western Australia, the Metropolitan Water Authority has since 1981 carried out a pilot investigation in recharging groundwater with secondary municipal wastewater using a rapid infiltration system at Canning Vale (Rule 1981). One million liters per day of wastewater is applied through six 40 m x 20 m basins located on fine to medium grain silica sand. The natural water table is about 9 m below the basins. Cycles of flooding and drying of the basins are used following the practice at the Flushing Meadows project. With cycles ranging from 9 days of flooding and 5 days of drying to 5 days of flooding and 9 days of drying no nitrogen removal was observed; only nitrification took place. Experiments using soil columns packed with sand from the recharge site also showed that no nitrogen was removed, and moreover substantial leaching of ammonium was observed (Mathew et al., 1982).

The above experience led us to develop a model that would bring together the contribution of all the variables in the processes leading to nitrogen removal in the vadose zone with cycles of wetting and drying, so that we could assess the operating conditions under which nitrogen could be removed, and hence explain why nitrogen removal did not take place in a particular case; and when nitrogen was removed, obtain the operating conditions that would optimize its removal.

This paper describes the development of the model, the assumptions and simplification used to obtain a solution to the model equations, and its application in predicitng nitrogen removal as a function of soil type and operating conditions.

MODEL FOR NITROGEN REMOVAL

A comprehensive model for the removal of ammonium (the major form of nitrogen in primary and secondary municipal wastewater) should include:

(a) Adsorption of ammonium by soil under changing soil moisture content incorporating the transport of ammonium in the soil solution due to convection and hydrodynamic dispersion, and the transfer of ammonium from the solution to the soil at a rate governed by the adsorption isotherm and the infiltration rate of the wastewater through the soil.

(b) Nitrification with a changing population of nitrifying bacteria which is dependent on the concentration of ammonium in the soil, soil pH and temperature, and the availability of oxygen as a function of depth below the soil surface.

(c) Leaching of nitrate from the soil to the solution, which is dependent on the water content of the soil during wastewater percolation, infiltration rate and the rate of hydrodynamic dispersion.

(d) Denitrification under changing populations of denitrifying bacteria; its rate is dependent on the availability of organic carbon to the denitrifiers.

We have mathematically formulated a model incorporating all the above factors, but it has been difficult to obtain the solution to the set of equations describing the model. We have found that a simplified model (i.e., disregarding factors which have small effects and making simplifying assumptions to restrict the values of certain variables) is adequate in providing answers that are useful for the management of nitrogen removal in a groundwater recharge scheme using treated wastewater (Mathew *et al.*, 1982).

The following assumptions and simplifications are used, based on batch and column experiments using a sandy loam (Pyrton): (i) nitrification takes place in the *top one meter* of soil only. In the field, nitrifiation is limited by the availability of oxygen, due to the decreasing oxygen availability with increasing depth. A depth of one meter has been chosen based on observation of air penetration in the sandy loam soil following the cessation of flooding. In heavier soils this depth may be considerably less. (ii) Nitrification follows Michaelis-Menten kinetics and proceeds uniformly along the one meter depth of the soil. The pH of the soil is between 6 and 7.5 and soil temperature is between 15 and 35° C ensuring a reasonable rate of bacterial activity. (iii) Hydrodynamic dispersion plays a minor role and soil ammonium equilibrium concentration is reached rapidly. As a consequence the concentration of ammonium down the soil is uniform. (iv) As the wetting front moves down the soil, resaturation is reached quickly. (v) Nitrate is leached rapidly and moves along with the wetting front. (vi) Denitrification is not limited by the availability of organic carbon in the first *four meters* of soil depth. It is considered that beyond a depth of four meters organic carbon would have been reduced to a concentration that will limit denitrification. The choice of depth is rather arbitrary, but takes into account depletion of organic carbon with depth due to its consumption by other bacteria.

The simplified model highlights two processes that basically determine the overall rate and hence efficiency of nitrogen removal: nitrification and denitrification. It is not difficult to understand why these two are the rate controlling processes since they are dependent on bacterial activity. Since the nitrifying and denitrifying bacteria are ubiquitous, the only requirement is an adequate capacity of the soil to adsorb ammonium. The minimum adsorption capacity that a soil must have can in fact be determined from the two rate controlling processes.

Nitrification

Following McLaren (1970) the oxidation of ammonium by bacteria can be expressed by:

$$K \ln (s/s_o) + (s - s_o) = k_a m_a t \qquad (1)$$

where K = saturation constant = 8 ppm (Ardakani et al,. 1974);
s = ammonium concentration; s_o = initial concentration;
k_a = a constant which has to be determined experimentally;
m_a = average biomass of bacteria.

Denitrification

A zero order kinetics has been used based on published results and the results of our laboratory batch tests.

$$(s - s_o) = k_d t_d \qquad (2)$$

where s denotes nitrate concentraion, k_d the denitrification rate and t_d is the time of travel of the wastewater from the surface to the water table.

Model parameters

Parameters for the model are obtained from the literature and from laboratory experiments using Pyrton sandy loam (Mathew et *al.*, 1982).

m_a = 4.0 x 10^3 organisms/g of soil
k_a = 7.0 x 10^{-4} ppm g organism^{-1} day^{-1}
k_d = 4.0 ppm day^{-1}

Ammonium adsorption isotherm: s (ppm) = 1.34 c (ppm) + 19.4.

APPLICATION OF MODEL

Determination of optimum flooding and drying periods

Consider the Pyrton sandy loam which adsorbs 47 ppm N when in contact with wastewater containing 20 ppm ammonium-N. For a reduction in N of 30 ppm in the soil, a drying period of about 10 days is required (Equation 1). With a renewed adsorption capacity of 30 ppm the amount of wastewater that can be applied without ammonium reaching the groundwater is 2.25 m^3/m^2 of basin area.

The minimum time required to denitrify 30 ppm N is 7.5 days (Equation 2). The maximum infiltration rate to ensure a liquid residence time of at least 7.5 days over 4 m of travel is 0.22 m/day. With the amount of wastewater applied (2.25 m/day) the flooding period is 10.2 days, which is satisfactory since it is greater than 7.5 days.

Thus a flooding period of 10 days and a drying period of 11 days (a 3 week cycle) with an infiltration rate of 0.22 m/day can be used as initial trial values in a field operation.

Effect of infiltration rate

With a given soil the desired infiltration rate may not be achieved. If the soil hydraulic conductivity is too low, the site is not suitable. If the soil hydraulic conductivity is too high, clay incorporation into the soil (to a depth of 1 m say) is possible. The effect of increasing infiltration rate beyond the optimum is nitrate leaching to groundwater as illustrated in Figure 1.

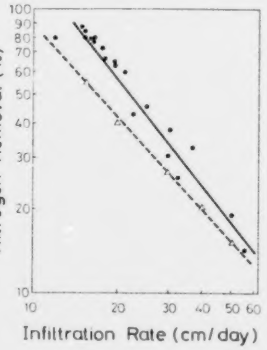

Figure 1. Effect of infiltration rate on nitrogen removal from sewage water by soil percolation. Solid line is the experimental curve of Lance et *al* (1976). Dotted line is obtained from the simplified model.

Minimum soil adsorption capacity

The effect of using shorter drying periods is shown in Table 1. Shorter drying periods result in a reduced renewed adsorption capacity. Consequently the flooding period must be short to prevent ammonium reaching the groundwater. The short flooding period is not sufficient in practice for anaerobic conditions to develop to allow denitrification at the desired rate. The results in Table 1 suggest that a renewed adsorption capacity of 20 ppm with an initial soil N concentration of 40 ppm is the minimum required. Our laboratory experiments indicate that a soil with a minimum cation exchange capacity of 5 meq/100 g is required.

TABLE 1

OPERATIONAL PARAMETERS FOR DIFFERENT RENEWED ADSORPTION CAPACITY VALUES

Operational parameters	Renewed adsorption capacity ppm *				
	50	40	30	20	10
1. Quantity treated per cycle m^3/m^2	3.75	3.00	2.25	1.50	0.75
2. Drying period, days	19	15	11	7.5	3.6
3. Time required for denitrification, days	11.4	9.1	6.8	4.5	2.2
4. Infiltration rate, m/day	0.35	0.44	0.59	0.88	1.82
5. Darcy velocity, m/day	0.15	0.19	0.25	0.37	0.77
6. Flooding period, days	25	16	9	4	0.97
7. Total period for a cycle, days	44	31	20	11.5	4.5

* Initial soil concentration = 100 ppm.

Approach to steady state

When starting the operation of recharge basins or changing operating conditions the model shows that steady state is reached only slowly. Table 2 shows that steady state is reached only after 7 cycles (140 days) when an operation with a flooding period of 9 days, drying period of 12 days and infiltration rate of 0.4 m/day is changed to flooding for 6 days, drying for 14 days and and infiltration rate of 0.35 m/day.

TABLE 2

NITROGEN REMOVAL PROCESSES LEADING TO STEADY STATE

Operational parameters	Flooding and Drying Cycle						
	I	II	III	IV	V	VI	VII
1. Adsorbed NH_4^+-N, ppm	45.2	41.5	36.6	35.4	34.5	34.2	34
2. Amount of NH_4^+-N to groundwater, g/m^2	6.7	1.5	0.25	0.1	0.02	0	0
3. Soil NH_4^+-N at the end of drying, ppm	13.5	8.6	7.5	6.5	6.2	6	6
4. Amount nitrified, ppm	31.7	30	29.1	29.9	28.3	28.2	28
5. Amount of NO_3^--N to groundwater, g/m^2	15.5	12.9	11.6	11.3	10.6	10.2	9.9
6. Percentage N removal	44	66	72	73	75	76	76.5

DISCUSSION

The model, though involving many simplifying assumptions, provides a means of comparing nitrogen removal under different operation conditions. It explains why the silica sand at Canning Vale in Perth does not remove ammonium. This is because the sand has very little adsorption capacity. The high hydraulic conductivity keeps the sand aerobic and hence only nitrification occurs. The situation is similar to the rapid infiltration system in Boulder, Colorado (Smith et *al.*, 1979). In Flushing Meadows, where the soil has some capacity to adsorb ammonium, short flooding and drying periods resulted in nitrification only. In this case the ammonium adsorption capacity of the soil was not exhausted during flooding, and the ammonium was completely nitrified during the drying period. No ammonium therefore reached the groundwater, but the flooding period was too short for an aerobic condition to be developed.

Continuous flooding at the basin at Milton, Wisconsin (Benham-Blair 1979) resulted in ammonium ions contaminating groundwater, since the adsorption capacity of the soil was not renewed by nitrification.

Two weeks of flooding and two weeks of drying resulted in ammonium in groundwater after a period of time at the Flushing Meadows Project (Bouwer *et al.*, 1980). Then a shorter period of flooding with a reduced application rate reduced the ammonium contamination significantly. The reduced application of the wastewater, hence ammonium applied, became more equal to the amount of ammonium nitrified during the drying period. The experience at Flushing Meadows Project also shows that it took a long time for the overall process to reach steady state after a change of operating conditions (of the order of one year).

In column experiments using 1 m of Pyrton sandy loam on top of silica sand we found that nitrogen was removed with a series of flooding and drying. The rate of removal as a function of flow rate was less than indicated in Figure 1, since the wastewater was partly nitrified.

CONCLUSIONS

The removal of ammonium from treated wastewater by soil application using a rapid infiltration system involves adsorption, nitrification, leaching and denitrification, which interact in a complex manner. The use of a simple model has enabled us to understand the interctions between the processes to arrive at optimum operating conditions and to amend the soil for even greater nitrogen removal.

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TRANSPORT OF HALOGENATED ORGANIC COMPOUNDS WITH SATURATED GROUNDWATER FLOW

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ABSTRACT

A one-dimensional model incorporating the mechanisms of advective flow, axial dispersion, liquid-phase mass transfer, local adsorption, equilibrium, and diffusion into aggregates is developed and solved using orthogonal collocation. The model is used to simulate the breakthrough of trichloroethylene in a packed column of sandy loam soil. Parameters for the model are derived from literature correlations, the column geometry, soil adsorption isotherms, kinetics studies, and breakthrough curves. The results show that dispersion and particle aggregation play a significant role in the spreading of chemical in one-dimensional flow.

INTRODUCTION

The proper design of land disposal sites and the assessment of groundwater contamination require the description of the transport and transformations of organic chemicals within soil matrices and geological formations. This paper describes the development of a one-dimensional model to simulate the movement of trace levels of organic chemicals with saturated groundwater flow. To demonstrate the modeling procedure, model simulations are compared to the breakthrough of toxic organic chemicals in laboratory soil columns.

MODEL DEVELOPMENT

For modeling purposes, the soil is divided into stationary and mobile phases. The stationary phase consists of aggregated soil particles which are of uniform size and spherically-shaped as shown in Figure 1. Both the solid soil matrix and fluid which is contained in the pores of the stationary phase are included in the mass balances. The mobile phase consists of the fluid that travels around the aggregates. The concentrations in the stationary phase are functions of radial and axial position and the concentrations in the mobile phase are functions of axial position.

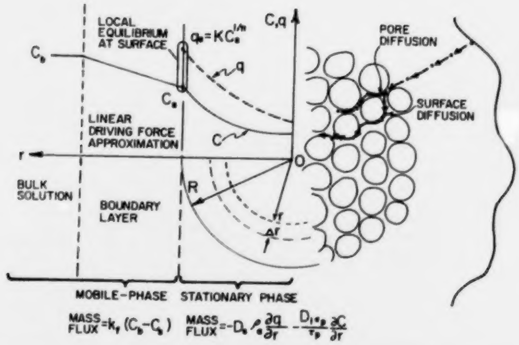
LOCAL EQUILIBRIUM AT SURFACE
$q_s = KC_s^{1/n}$
C,q
PORE DIFFUSION
C_b
q
C_s
SURFACE DIFFUSION
LINEAR DRIVING FORCE APPROXIMATION
C
r
O
BULK SOLUTION
BOUNDARY LAYER
R
r
Δr
MOBILE-PHASE
STATIONARY PHASE
MASS FLUX $= k_f (C_b - C_s)$
MASS FLUX $= -D_s \rho_a \frac{\partial q}{\partial r} - \frac{D_l \epsilon_p}{\tau_p} \frac{\partial C}{\partial r}$

Figure 1. Model mechanisms for mass transfer into spherical aggregates.

The following mechanisms are incorporated into the model: (a) advective flow, (b) axial dispersion, (c) liquid-phase mass transfer resistance from the mobile to stationary phase, (d) local adsorption equilibrium between the solute adsorbed onto the soil matrix surface and the solute in the intrastationary fluid, and (e) both surface and pore diffusion as the intraaggregate mass transport mechanisms. The mobile phase mass balance in dimensionless form is:

$$\frac{1}{(1 + D_g)} \frac{\partial \bar{C}_b(\bar{z},T)}{\partial T} = \frac{1}{Pe} \frac{\partial^2 \bar{C}_b(\bar{z},T)}{\partial \bar{z}^2} - \frac{\partial \bar{C}_b(\bar{z},T)}{\partial \bar{z}} - 3St(\bar{C}_b(\bar{z},T) - \bar{C}(z,T)) \qquad (1)$$

The terms which appear in the equation account for accumulation in the mobile liquid phase, axial dispersion and diffusion, advective flow, and transport from the mobile to the stationary phase by liquid phase mass transfer. The initial condition is:

$$\bar{C}_b(0<\bar{z}\leq 1,\ T=0) = 0 \qquad (2)$$

and the boundary conditions for the mobile phase are those proposed by Danckwerts (1953):

$$\bar{C}_I(\bar{z}=0,T) - \bar{C}_b(\bar{z}=0^+,T) = \frac{1}{Pe} \frac{\partial \bar{C}_b(\bar{z}=0^+,T)}{\partial \bar{z}} \qquad (3)$$

$$\bar{C}_I(\bar{z}=0,T) - \bar{C}_b(\bar{z}=1,T) = \frac{1}{(1+D_g)} \frac{d}{dT}\left[\int_0^1 \left[\bar{C}_b(\bar{z},T) + 3D_g \int_0^1 \bar{q}'(\bar{r},\bar{z},T)\bar{r}^2 d\bar{r}\right] d\bar{z}\right] \qquad (3b)$$

$$\frac{\partial \bar{C}_b(\bar{z}=1,T)}{\partial \bar{z}} = 0 \qquad (4)$$

$$\frac{\partial^2 \bar{C}_b(\bar{z},T)}{\partial T \partial \bar{z}} = 0 \quad \text{and} \quad \frac{\partial \bar{C}_b(\bar{z},T=0)}{\partial \bar{z}} = 0 \qquad (4b)$$

Equations 3 and 4 are derived from equating the mass flux entering and leaving the bed assuming dispersion and diffusion exist only in the bed. Equations 3b and 4b are equivalent alternatives to Eqs. 3 and 4 which were used in the numerical solution.

The stationary phase mass balance is:

$$E_d \frac{(1 + D_g)}{D_g} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}}\left[\bar{r}^2 \frac{\partial \bar{q}'(\bar{r},\bar{z},T)}{\partial \bar{r}}\right] = \frac{\partial \bar{q}'(\bar{r},\bar{z},T)}{\partial T} \qquad (5)$$

The first term which appears in Equation 5 accounts for both pore and surface diffusion, and the second term accounts for accumulation in the intrastationary phase fluid and solid surfaces. The initial condition is:

$$\bar{q}'(0\leq\bar{r}\leq 1,\ 0\leq\bar{z}\leq 1,\ T=0) = 0 \qquad (6)$$

The boundary conditions are:

$$\frac{\partial \bar{q}'(\bar{r}=0,\bar{z},T)}{\partial \bar{r}} = 0 \qquad (7)$$

$$Bi(\bar{C}_b(\bar{z},T) - \bar{C}(\bar{z},T)) = \frac{\partial \bar{q}'(\bar{r}=1,\bar{z},T)}{\partial \bar{r}} \qquad (8)$$

$$\frac{St(1 + D_g)}{D_g}(\bar{C}_b(\bar{z},T) - \bar{C}_s(\bar{z},T)) = \frac{\partial}{\partial T} \int_0^1 \bar{q}'(\bar{r},\bar{z},T)\bar{r}^2 \partial \bar{r} \qquad (9)$$

Equation 7 results from symmetry. In Equation 8, the liquid phase mass flux from the mobile phase is equated to the stationary phase mass flux. Equation 9 equates the mass transfer from the mobile to that accumulated in the stationary phase and this equation, which is redundant, is used in the numerical algorithm.

Since solute at the external boundary of the stationary phase fluid is assumed to be in equilibrium with that adsorbed onto the surface, the concentration on the surface is related to the liquid phase concentration by adsorption equilibrium equations such as the Freundlich equation:

$$\bar{q}' = \frac{\varepsilon_p \bar{C} + \left[\rho_a K C_o^{1/n-1}\right]\bar{C}^{1/n}}{\varepsilon_p + \left[\rho_a K C_o^{1/n-1}\right]} \qquad (10)$$

Equations 1 through 10 represent a set of simultaneous, nonlinear, partial differential equations that can be solved numerically by orthogonal collocation (OC) (Finlayson, 1980). Figure 2 gives a sample grid for the application of OC for 2 internal collocation points for both the axial and radial directions. Typically, more collocation points were used to obtain the desired accuracy. Applying OC to Eqs. 5 and 9 gives the following set of ordinary differential equations (ODEs) at the collocation points for the immobile phase:

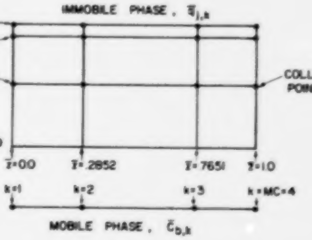

Figure 2. Location of orthogonal collocation points in the axial and radial directions for two internal points.

$$\frac{d\bar{q}'_{jk}(T)}{dT} = \frac{D_g+1}{D_g} E_d \sum_{i=1}^{NC} B^r_{ji}\, \bar{q}'(T)_{ik}$$

Valid for Radial Points j=1 to NC-1 and Axial Points k=1 to MC (11)

$$\frac{d\bar{q}'_{NC,k}(T)}{dT} = \frac{(D_g+1)}{W^r_{NC} D_g} St(\bar{C}_{b,k}(T) - \bar{C}_{s,k}(T)) - \sum_{i=1}^{NC-1} \frac{W^r_i}{W^r_{NC}} \frac{d\bar{q}_{ik}(T)}{dT}$$

Valid for k=1 to MC (12)

Eqs. 11 and 12 are valid for all axial locations 1 through MC. Applying OC to Eqs. 1, 3b and 4b yields the following ODEs for the mobile phase:

$$\frac{d\bar{C}_{b,k}(T)}{dT} = (D_g+1) \sum_{i=1}^{MC} \left[\frac{B^z_{ki}}{Pe} - A^z_{ki}\right] \bar{C}_{b,i}(T) - 3St(D_g+1)(\bar{C}_{b,k}(T) - \bar{C}_{s,k}(T)$$

Valid for Axial Points k=2 to MC-1 (13)

PARAMETER EVALUATION

The physical and chemical parameters listed in Table 1 are used to compare the soil column model solution to the breakthrough of trichloroethylene (TCE) in a laboratory soil column. These parameters were derived from data collected on soil columns packed in our laboratory, from literature correlations, from measurements of the dispersion of chloride, and from batch soil adsorption equilibrium and kinetics tests. The median size and uniformity coefficient were determined from the soil's particle size distribution. Porosity and column length were derived from the physical geometry of the soil column and the hydraulic conductivity and specific discharge were measured during breakthrough experiments with the packed column.

TABLE 1. SOIL COLUMN PARAMETERS

Organic Chemical	Trichloroethylene
Soil	Keweenaw 7, B horizon, sandy loam
Median Size	0.011 cm
Porosity	0.439
Particle Density	2.59 g/cm^3
Column Length	30.48 cm
Hydraulic Conductivity	0.00265 cm/s
Specific Discharge (u)	0.00146 cm/s
Temperature	10°C
Liquid Diffusion Coefficient (D_l)	6.2 x 10^{-6} cm^2/s
Mobile-phase Mass Transfer Coefficient (k_f)	4.6 x 10^{-4} cm/s
Dispersion Coefficient (E)	1.9 x 10^{-3} cm^2/s
Influent Concentration (C_o)	404 ug/L
Freundlich Isotherm Capacity (K)	1.62
Freundlich Isotherm Intensity (1/n)	0.94
Aggregate Radius (R)	0.11 cm

The liquid diffusion coefficient for TCE was estimated by the Hayduk and Laudie correlation (loc. cit., Reid, Prausnitz, and Sherwood, 1977). The mobile-phase mass transfer coefficient was calculated from a correlation developed by Wilson and Geonkoplis (1966) for very low Reynolds numbers in packed beds. Dispersion was derived from the product of the Reynolds and Schmidt numbers using a correlation presented by Fried (1975). The diffusivity within aggregates was estimated by assuming that the intraaggregate diffusive transport is due to pore diffusion. The tortousity within the aggregate was assumed to be the same as for the mobile-phase and, according to Fried (1975), it should be equal to 0.67.

Figure 3 presents the results of a batch rate study along with a model prediction of the batch rate data when liquid-phase mass transfer resistance is the sole rate-limiting mechanism. These results indicate that the assumption of local equilibrium is valid for this particular system since there appear to be no slow surface reactions and no diffusion into surface carbon.

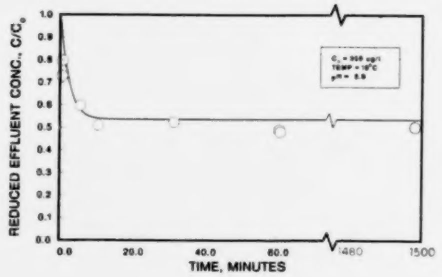

Figure 3. Batch rate kinetics for trichloroethylene onto Keweenaw 7B soil. The open circles are the data points and the solid line is a model prediction assuming that liquid-phase mass transfer resistance is the rate-limiting mechanism.

The adsorption of TCE onto Keweenaw soil was determined by soil adsorption isotherm experiments. Varying concentrations of TCE ranging from 0 to 600 ug/L were mixed with soil in headspace-free bottles for one day. Once the mixture had achieved equilibrium, the soil and solution were separated by centrifugation and the solution was extracted into isooctane for gas chromatography analysis. A least squares regression of the logarithms of the isotherm data shown in Figure 4 gave best fit values of 1/n and K of 0.69 and 6.5 with 95% confidence intervals of 0.61 to 0.77 and 4.6 to 9.2, respectively.

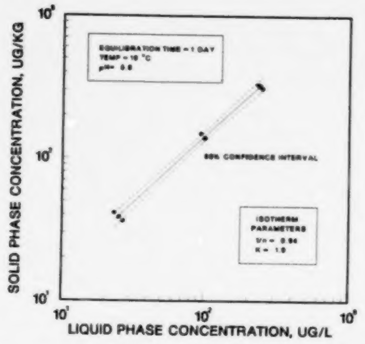

Figure 4. Soil adsorption isotherm for trichloroethylene onto Keweenaw 7B soil.

A miscible displacement soil column experiment was conducted at the velocity, porosity, temperature, and column length listed in Table 1. An airtight soil column apparatus constructed of glass, teflon, and stainless steel was packed with Keweenaw soil and a solution containing TCE was pumped through the column to give the breakthrough and elution of the chemical. These results along with model simulations using the parameters listed in Table 1 are presented in Figure 5. All parameters except aggregate diameter were determined by independent experiments or from literature correlations. Initially, we tried to account for the shape of the TCE breakthrough curve by assuming that spreading was done to dispersion around uniform particles (Fried, 1975) and adsorption alone; however, a very sharp breakthrough of chemical is predicted as shown in Figure 5. Similar results were obtained when only the mechanisms of nonlinear adsorption, dispersion, and liquid-phase mass transfer resistances were included. Only when we assumed that diffusion into the stationary fluid of aggregates occurred, could we account for the spreading of the TCE breakthrough curve. Based on this model calibration, the aggregate diameter is 0.22 cm which when compared to the median particle size of 0.011 cm demonstrates that considerable aggregation occurs even in packed soil columns.

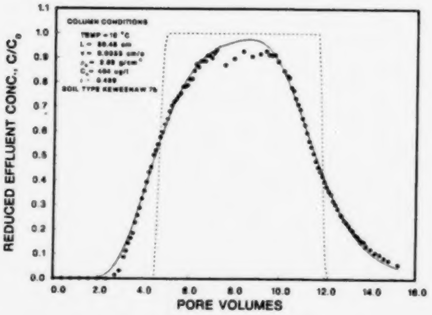

Figure 5. Breakthrough of trichloroethylene through a packed column of Keweenaw 7B. The solid line is a model prediction using all the parameters listed in Table 1. The dashed line is a model prediction assuming adsorption and dispersion around uniform particles.

These results show that the modeling approach presented here gives reasonable simulations when adjusted for aggregate size. We are working to develop laboratory procedures that will independently measure aggregate diameter in order to test the predictive capability of the soil column model.

NOMENCLATURE

Roman Letters

A_{kl}^{z} = orthogonal collocation matrix that approximates the first derivative in the axial direction

Bi = $(1-\epsilon)k_f R/(\epsilon D_s' D_g)$; Biot number, which is the ratio of external liquid-phase mass transfer rate to the intra-stationary phase rate, (dimensionless)

B_{kl}^{r} = orthogonal collocation matrix that approximates the Laplacian quadrature in the radial direction

B_{kl}^{z} = orthogonal collocation matrix that approximates the Laplacian quadrature in the axial direction

$C_b(z,t)$ = bulk fluid-phase concentration in mobile phase as a function of axial position and time (M/L^3)

$\bar{C}_b(\bar{z},T)$ = $C_b(\bar{z},T)/C_0$

$\bar{C}_1(\bar{z},T)$ = $C_b(\bar{z}=0^-,T)/C_0$

$C_s(z,t)$ = fluid-phase concentration in micropores of stationary phase as a function of radial and axial position and time (M/L^3)

$\bar{C}_s(\bar{z},T)$ = $C_s(\bar{z},T)/C_0$

C_0 = arbitrary concentration used to normalize dimensionless equations (M/L^3)

D_g = $(1-\epsilon)(\epsilon_p C_0 + \rho_a q_e)/(\epsilon C_0)$; solute distribution ratio, which is the ratio of the adsorbate in the intra-stationary phase to that in the mobile phase at equilibrium and C_0 (dimensionless)

D_l = liquid diffusion coefficient (L^2/t)

D_p = D_l/T_p; intra-aggregate pore diffusion coefficient (L^2/t)

D_s = intra-aggregate surface diffusion coefficient (L^2/t)

D_s' = $(D_p\epsilon_p + D_s\rho_a K_{ave})/(\epsilon_p + \rho_a K_{ave})$; effective intra-aggregate diffusion coefficient (L^2/t)

E = axial dispersion and diffusion coefficient (L^2/t)

E_d = $LD_g D_s'/vR^2$; surface diffusion modulus, which is a measure of the ratio of the mass transfer zone length (which is due to stationary phase mass transfer resistance) to the bed length (dimensionless)

K = Freundlich isotherm capacity constant $(L/M)^{1/n}$

K_{ave} = $nKC_0^{1/n-1}$; average Freundlich isotherm capacity constant (L/M)

k_f = film transfer coefficient (L/t)

L = length of column (L)

MC = number of collocation points in the axial direction

1/n = Freundlich isotherm intensity constant (dimensionless)

NC = number of collocation points in the radial direction

$q'(r,z,t)$ = stationary-phase concentration including solute in pore water and adsorbed on soil surface as a function of radial and axial position and time (M/M)

$\bar{q}'(\bar{r},\bar{z},T)$ = $q'(\bar{r},\bar{z},T)/q_e(T)$ (dimensionless)

$q_e(t)$ = $KC_0^{1/n} + \epsilon_p C_0/\rho_a$; stationary-phase concentration in equilibrium with C_0 (M/M)

Pe = vL/E; Peclet number (dimensionless)

R = radius of aggregated particle (L)

r = radial coordinate (L)

$\bar{r}$ = r/R (dimensionless)

St = $(1-\epsilon)k_f L/(\epsilon v R)$; Stanton number, which is a measure of the ratio of the mass transfer zone (length which is due to liquid-phase mass transfer resistance) to the bed length (dimensionless)

t = elapsed time (t)

v = average interstitial velocity in macropores (L/t)

W_l^{r} = orthogonal collocation vector that approximates the Gauss quadrature in the radial direction

W_l^{z} = orthogonal collocation vector that approximates the Gauss quadrature in the axial direction

z = axial coordinate (L)

$\bar{z}$ = z/L (dimensionless)

Greek Letters

ϵ = macropore void fraction of column (dimensionless)

ϵ_p = micropore void fraction of stationary phase (dimensionless)

ρ_a = aggregate particle density which includes micropore volume (M/L^3)

T = $tv/L(1+D_g)$; throughput, which is the ratio of mass of solute fed to the column to the mass of solute in a column saturated to capacity (dimensionless)

ACKNOWLEDGEMENT

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A MODEL TO EVALUATE SALT WATER INTRUSION DUE TO DIFFERENT CONJUNCTIVE USE STRATEGIES IN COASTAL AQUIFERS IN SAUDI ARABIA

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ABSTRACT

A study was conducted to evaluate different strategies of conjunctive use management of surface and groundwater in the coastal aquifers of the Red Sea coast in Saudi Arabia. A physically based distributed parameter model was developed to simulate both the physical behavior and the operational behavior of the surface-groundwater system. The numerical model developed was based on the "Discrete Kernel Approach" of groundwater modeling (a response matrix model). The development strategies tested were designed to use the groundwater as a supplementary source to the traditionally used surface supplies. The excessive extraction of groundwater may result in the mining of the aquifer and degradation of groundwater quality by the intrusion of sea water. A component of the model simulates the salinity transport at the coastal boundary of the aquifer. This paper presents the design of this model component and the procedures used in the coupling of the salinity transport model to the quantity flow model. A simple technique where the solute transport by hydrodynamic dispersion and convection were treated separately was used. The study results showed that the test strategies will not drastically effect the groundwater quality by seawater intrusion.

INTRODUCTION

A water resources investigation study was conducted to evaluate different strategies of conjunctive use management of surface and groundwater in the coastal aquifers of the Red Sea in Saudi Arabia. A pilot study area consisting of the wadi and the aquifer system of Wadi Jizan was selected for modeling and to conduct a case study. The derived conclusions of this case study will be useful and applicable in general for the future water resources planning and development in the other coastal wadi-aquifer systems in the region.

The project area covers the upper flood plains of the Wadi Jizan and consists of 22,000 hectares (54,000 acres). The average annual rainfall in the project area is about 200 mm. It has been observed that the rains generally fall on about 12 nonconsecutive days of the year, principally during the hottest months of July and August. The mean annual wadi surface flows were estimated at 79-83 million cubic meters per year. The principal aquifer of the Wadi Jizan area is comprised of a series of recent unconsolidated heterogeneous alluvial deposits consisting of gravel, sand, silt and clay. The aquifer thickness varies from a few meters near the laval flows in the east to about 100 meters in the center of the Jizan plain. The boundary to the western end of the aquifer is the Red sea. The water in the aquifer flows from east to west roughly paralleling the wadi bed. Estimated recharge to the aquifer is around 25 million cubic meters per year. It has been concluded that much of the recharge passes to the saline coastal marshes (sabkha). Estimates indicate evaporation from soil surface of the sabkha may exceed 50 million cubic meters per year.

The purpose of this study was to investigate methods of improving the agricultural system in the region by more effectively developing and managing the water resources. Realistic alternatives were sought and evaluated as to their effectiveness on improving the quantity, quality and dependability of water supplied to the area. Measurements of the performance of the alternative strategies are based on hydrologic (recharge, evidence of groundwater mining, change in water quality, etc.) and agricultural (satisfaction of crop needs, increased irrigated areas, etc.) considerations.

MODEL SPECIFICATIONS

Three basic components were identified in the physical system for the purpose of modeling its behavior. They are namely: the surface water conveyance system, the unsaturated zone of the aquifer, and the saturated zone of teh aqujifer. These components are in a continuous dynamic interaction. The physical system is subjected to natural and man-made excitations. For a realistic assessment of the test strategies, a number of variables which describe the resulting state of the physical system has to be simulated. Examples of such a state are: water table elevation in the aquifer, salinity levels of groundwater close to the coastal boundary, surface flows in the wadi, water availability in the farms, etc. A physically based distributed parameter model was developed. a detailed discussion on the design and application of the model is given in Illangasekare, et al., (1983) and Illangasekare and Morel-Seytoux (1984). The design of the component of this model which simulates the salt water intrusion into the aquifer is presented in this paper.

SIMPLE MODEL FOR SOLUTE TRANSPORT

A very limited amount of data was available to develop and calibrate the component of the model which describes the intrusion of salt water into the aquifer. In this study, the conclusions on the effectiveness of the strategies were reached based on the relative merits of the alternatives rather than on absolute quantitative values of the simulated state of the system. Hence, a simple technique based on realistic assumptions was used.

Three basic assumptions are made in the analytical formulation of the problem. First, it is assumed that the concentration of salt at the coastal boundary of the aquifer remains constant during the simulation. This is the concentration of salt in sea water. The second assumption is that close to the sea in the aquifer, the movement of salt by hydrodynamic dispersion and convective transport occur unidirectionally parallel to the longitudinal direction of the aquifer. This assumption of no lateral transport is justified by the fact that the groundwater flows approximately parallel to the longitudinal direction without any significant groundwater pumping close to the sea. Also, the sea acts as a constant line source along the lateral direction. The third assumption is that there is complete mixing in the vertical direction in the aquifer.

The equation describing the two-dimensional areal transport and dispersion of given nonreactive dissolved chemical species in flowing groundwater is given by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j}\right) - \frac{\partial}{\partial x_i} (v_i \; c) - W_i \qquad (1)$$

where c is the mass concentration of dissolved solids, D_{ij} is the coefficient of hydrodynamic dispersion (tensor), v_i is the seepage velocity in the direction x_i, and W_i is the mass flux of a source or sink. The theoretical basis and the derivation of Eq. 1 are discussed in detail in a number of books and publications (Bear, 1972; Reddel and Sunada, 1970; Bredehoeft and Pinder, 1973, etc.). The first term on the right hand side of Eq. 1 represents the movement of a solute due to hydrodynamic dispersion. The second term describes the mass flux of the solute transported by the average fluid motion of the groundwater.

The groundwater flow in the saturated zone of the aquifer is modeled by solving the linearized form of Boussineq equation. It has been shown previously (Illangasekare, et al., 1983) using the "Discrete Kernel" approach (Morel-Seytoux and Daly, 1975) the solution to the Boussineq equation is of the form:

$$h_i(n) = h_i^{o} + \sum_{\alpha=1}^{\pi} \sum_{\nu=1}^{n} \delta_{i\lambda}(n - \nu + 1)\, Q_\lambda(\nu) + \sum_{\alpha=1}^{\pi} \tau_{i\alpha}(n)\, h_\alpha^{o} \qquad (2)$$

where $h_i(n)$ is the water table elevation in a calculation cell i at the end of period n, h_i° is the initial water table elevation, $\sigma_{i\lambda}$ is the discretized response of water table in cell i due to a unit pulse pumping excitation in cell λ, Q_λ is the pumping excitation in cell λ, $\tau_{i\alpha}$ is a discretized kernel function which describes the evolution of the water table in cell i due to a unit change of initial head in cell α and π is the total number of calculation cells.

Separating the transport process into dispersive transport and convective transport is somewhat artificial as the two processes occur simultaneously. But in the simple model developed in this study, these processes are dealt with separately. The flux across the boundary of a calculation cell i due to hydrodynamic dispersion can be approximated in the finite difference form:

$$F_i^{(1)} = \frac{D_{i-\frac{1}{2}}}{\Delta\ell}\,[\bar{c}_{i-1} - \bar{c}_i] \qquad (3)$$

where $D_{i-\frac{1}{2}}$ is the coefficient of dispersion at the common boundary of cells i and i-l, $\bar{c}_i$ is the average concentration of solute in cell i during the simulation time step, and $\Delta\ell$ is the size of the cell. A similar expression can be written for the flux leaving the cell.

The convective transport across the cell boundary is a function of the rate of flow of water at the boundary. The flux entering a cell i is given by:

$$F_i^{(2)} = \bar{q}_{i-\frac{1}{2}}\,\bar{c}_{i-1} \qquad (4)$$

where $\bar{q}_{i-\frac{1}{2}}$ is the average rate of flow of water from cell i-l to i during the simulation time step. Similar expression can be written for the cases when the flow enters or leaves the ith cell through other cell boundaries. The average flow during a simulation period n is obtained using the water table elevations computed using Eq. 2. The average flow during the period is taken as the arithmetic mean of the flow at the beginning and the end of the period. Symbolically,

$$\bar{q}_{i-\frac{1}{2}} = \frac{1}{2}\,\frac{T_{i-\frac{1}{2}}}{\Delta\ell}\,[(h_{i-1}(n) + h_{i-1}(n-1)) - (h_i(n) + h_i(n-1))] \qquad (5)$$

where $T_{i-\frac{1}{2}}$ is the transmissivity at the cell boundary.

At the beginning of a simulation time step the solute concentrations within all calculation cells are known. The average concentration in a cell is taken as the arithmetic mean of the known initial concentration, $c_i(n-1)$ and the unknown final concentration, $c_i(n)$ at the end of the time step. Symbolically:

$$\bar{c}_i(n) = \frac{1}{2}\,[c_i(n-1) + c_i(n)] \qquad (6)$$

Applying the equation of mass conservation of the solute to each of the cells using Eqs. 3 and 4 to estimate the inflow or outflow of solute flux, a system of simultaneous equations is obtained. The solution to this system of equations gives the concentrations of solute in the calculation cells at the end of the simulation time step.

MODEL APPLICATION

The complete model of which the solute transport model is a component was calibrated using hydrologic and meteorologic data for the period 1953 through 1969. Five alternative conjunctive use strategies were simulated using the model. The reference run (REFERENCE 1) reproduce the hydrologic and agronomic system which currently exists in the study area. Two strategies were designed to supplement the surface supplies with groundwater. The first supplemental strategy (SUPPLEMENTAL 1) was designed to supply groundwater to 3790 ha of land in the lower parts of the study area which traditionally did not receive the full surface water rights. A total of 118 high capacity wells were located to supply 30.3 MCM per year. In the second supplemental strategy (SUPPLEMENTAL 2) the area receiving groundwater was reduced to 2584 ha. A total of 80 wells were operated.

Two strategies which combine an improved surface water distribution system and a scheme which supplies groundwater perennially to small farms which grow fruits, vegetables, and fodder crops were designed. In the first perennial scheme (PERENNIAL 1), the natural wadi inflows were used in conjunction with an improved flood spreading system. The improved flood spreading system consists of six permanent diversion structures across the wadi and a system of canals which delivers the flood water to the farms. The second perennial scheme (PERENNIAL 2) uses the same distribution system with the upstream inflows attenuated through a large upstream reservoir. In both the perennial schemes, groundwater was supplied to 1075 ha through 43 tube wells.

The salinity transport model was used to assess the impact of the development strategies on the salinity levels of groundwater in the aquifer.

RESULTS AND CONCLUSIONS

The model calculated the chloride concentration at the end of each simulation week at various distances from the coastline. The evolution of chloride content at the end of each year in a cell 5 kilometers away from the coastline is plotted on Fig. 1 as a function of time. Analysis of the computed chloride content values show that the salinity concentration at approximately 1 km from the sea steadily increased for all strategies. The SUPPLEMENTAL 1 strategy with the largest groundwater extraction resulted in a steady increase in salinity levels at all locations. For all the other strategies, the salinity levels significantly decreased at all locations 2 km or beyond from the sea. In general,

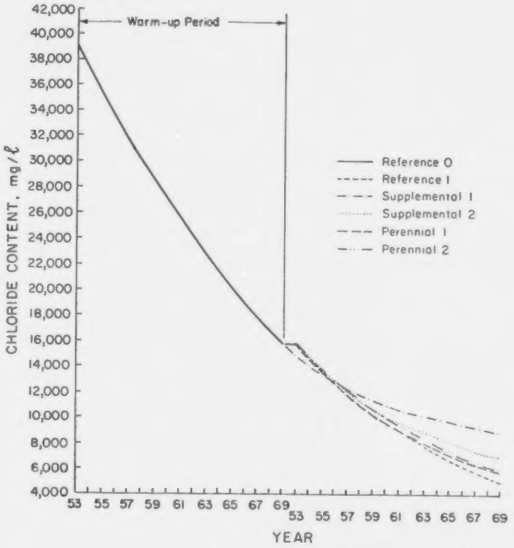

FIGURE I. CHLORIDE CONTENT AT LONGITUDINAL COORDINATE I=36 (APPROXIMATELY 5 KILOMETERS FROM COASTLINE)

the continuous decline in chloride concentration is interpreted as evidence that the rates of groundwater extraction for the various development strategies will not drastically affect the groundwater quality. Had wells been located in the coastal region or the extractions been large enough to cause the direction of fresh groundwater flow to reverse, drastic changes in chloride contents may have been observed.

This study demonstrated the application of solute transport model in a surface-groundwater conjunctive use study. The data limitations required the design of a simple model. The design procedure used in the coupling of this simple model to a groundwater quantity flow model was presented.

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AN IMPROVED NUMERICAL MODELLING OF CONTAMINANT TRANSPORT IN SATURATED AQUIFERS

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ABSTRACT

Contaminated discharge and run-off from landfills pose a problem to the groundwater quality. A strong need exists to evaluate the impact of present and proposed waste disposal sites on groundwater purity and the resulting effect on the public. The use of numerical models in the determination of the spread of contaminants will allow one to make advance predictions. The mathematical representation of the phenomena of mass transfer in porous media consists of two equations, a flow equation and a transport equation; the flow transport being represented by the stream function. Galerkin finite element technique is used to simulate the transport of contaminant in a two dimensional rectangular confined aquifer. The pollutant is assumed to discharge continuously from the top boundary of the aquifer. The spread of the contaminants at different time steps are determined to get the concentration isopleths. For a high degree of accuracy, a refined mesh near the contaminant source is recommended.

INTRODUCTION

The disposal of hazardous waste materials has now become a problem of great concern. The amount of hazardous waste materials placed in landfills has increased dramatically as a result of new and stricter regulations, better enforcement practices, and the ban on ocean dumping. Landfills present a potential problem for adjacent groundwater aquifers. Contaminated discharge and run-off from landfills with hazardous waste materials can pollute the groundwater. A strong need exists to evaluate the impact of present and proposed waste disposal sites on groundwater purity and the resulting effect on the public. As a result, the subject of mass transport of hazardous materials in the groundwater environment has received wide attention in the recent past and present.

This present investigation has used the Galerkin Finite Element technique to simulate the transport of contaminants in a two dimensional aquifer. The pollutant is assumed to discharge continuously from the top boundary of the aquifer due to leaky conditions. The mathematical model formulated and the methodology of study are presented in the following sections.

MATHEMATICAL FORMULATION

The mathematical model to describe the mass transport of a fluid through a saturated porous medium is formulated upon two equations, a flow equation and a transport equation. These two equations are coupled by the density and velocity terms. The flow equation for a mixture of miscible fluids is derived by combining the law of conservation of mass, Darcy's Law and an equation of state. The derivation of this flow equation is presented here.

Continuity Equation

The continuity equation of flow as given by Reddell and Sunada (1970) (2) is based on the conservation of mass. At a fixed point in time, for a differential element, (Rate of mass inflow) -(Rate of mass outflow) ^{5} (Rate of change of mass inside the element). Therefore, continuity Equation is

$$\frac{\partial}{\partial X_\alpha} (\rho q_\alpha) - \rho^1 W = 0 \tag{1}$$

where p = fluid mass density of solution $(\frac{M}{L^3})$

q_α; $(\frac{Q_{\alpha\beta}}{\Delta A}, Q_{\alpha\beta} = 0, \chi B)$ Components of discharge Velocity (L/T)

p^1 = mass density of source or sink fluid within the element (M/L^3)

W = rate of production of source or sink. Positive when a source and negative when a sink. (L/T)

Dispersion Equation

A convective-dispersion equation is obtained from the conservation of mass as (1, 5)

$$\frac{\partial}{\partial X_\alpha} (D_{\alpha\beta} \frac{\partial C}{\partial X_\beta}) - \frac{\partial}{\partial X_\alpha} (V_\alpha C) - \frac{C^1 W}{\epsilon} = \frac{\partial C}{\partial t} \tag{2}$$

where

C = Concentration of fluid (M/L^3)
V_α = Components of Seepage Velocity (L/T)
C^1 = Source or Sink fluid concentration (M/L^3)
ϵ = Porosity
$D_{\alpha\beta}$ = Dispersion Coefficient (L^2/T). It has been treated as a scalar in this study.

Darcy's Equation

Because of the interrelationship among several of the parameters in equations 1 and 2, the following auxillary equation is needed in the mathematical model. The components of the velocity for the fluid mixture are obtained from the generalized Darcy's equation, as

$$V_\alpha = - \frac{K_{\alpha\beta}}{\epsilon\mu} (\frac{\partial P}{\partial X_\beta} + \rho g_\beta) \tag{3}$$

where

$K_{\alpha\beta}$ = Components of permeability tensor (l^2)
μ = Dynamic Viscosity (M/LT)
V_α = Components of pore velocity (L/T)
P = Pressure (M/LT^2)
g_β = Components of Gravity (L/T^2)

Finite Element Technique

Using an isoparametric four noded element as shown in Figure 1, and assuming the shape function to be linear, the continuity equation and Darcy's equation are reduced to algebraic equations using the Galerkin's technique of method of weighted residuals and are written symbolically in the matrix form as (4)

$$[H] \{II\} + \{F\} = 0 \tag{4}$$

where [H] is an array of order 3n x 3n, {II} and {F} are arrays of order 3n x 1. In this flow equation (4), the pressure and velocity components are solved for each node. The dispersion equation (3) when written in matrix form is

$$[N] \{C\} + [M] \frac{d\{C\}}{dt} + \{F\} = 0 \tag{5}$$

where {C} and {R} are arrays of order n x 1. [N] and [M] are coefficient matrices or order n x n. The dispersion equation has the general form of a propagation problem of first order ordinary differential equation, wherein spatial dependence of variables is carried by the finite element approximation in the coefficient matrices [M] and [N] and the vector {R} contains known information from boundary conditions.

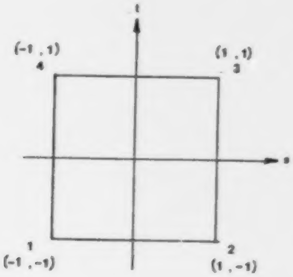

Figure 1. A Two-Dimensional Linear Isoparametric Quadrilateral Element in S-t Plane.

Temporal Approximation

The time derivative term in Equation (5) can be approximated by employing the direct integration method of a weighted finite difference, and the equation (5) can be rewritten as

$$[\dot{N}] \; (\theta\{C\}_{t+\Delta t} + (1-\theta)\{C\}_t) + \frac{1}{\Delta t}[M](\{C\}_{t+\Delta t} + \{C\}_t) = \theta\{-R\}_{t+\Delta t} + (1-\theta)\{-R\}_t \tag{6}$$

in which θ is a scalar parameter. Employing a fully implicit method with $\theta = 1$ and thus guaranting stability, equation (6) now yields as

$$([N] + \frac{1}{\Delta t}[M])\{C\}_{t+\Delta t} = \frac{1}{\Delta t}[M]\{C\}_t - R \tag{7}$$

An additional equation is required to update the mass density of the solution after each time step, namely an equation of state

$$\rho = \rho_W + EC \tag{8}$$

where

ρ_W = mass density of fresh water
E = a weighting constant to redistribute the variable concentration of contaminant.

PROBLEM DEFINITION

The phenomenon of contaminant transport in porous media is investigated for a two dimensional, saturated, rectangular, confined aquifer as shown in Figure 2. The pollutant is assumed to discharge continuously from the top boundary of the confined aquifer due to leaky conditions. It is assumed that the leakage occurs over a length of d/8 where d is the depth of the aquifer. Mass transport in the unsaturated zone is considered to be neglible. The dimensions and boundary conditions (3) utilized in this problem are shown in Figure 3.

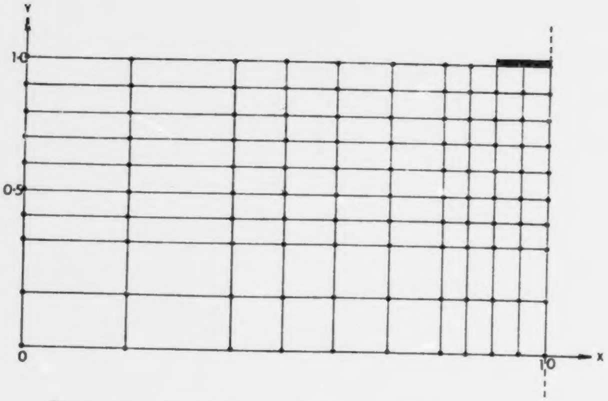

Figure 2. Finite Element Discretizations of the Rectangular Aquifer-Half Section - With 90 Elements and 99 Nodal Points.

The location of the center of the source, for convenience is kept at a nondimensional distance of 10 (X/d = 10) from the left hand boundary. The depth of the aquifer is assigned a range of 1 to 20. The investigation is carried out with the mesh sizes presented in Figure 2.

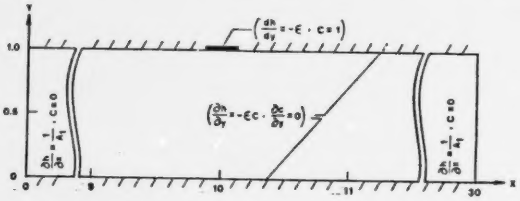
Y
$\left(\frac{dh}{dy} = -\epsilon \cdot c = 1\right)$
1.0
0.5
0
$\frac{\partial h}{\partial x} = -\frac{1}{\epsilon} \cdot C = 0$
$\left(\frac{\partial h}{\partial y} = -\epsilon c \cdot \frac{\partial c}{\partial y} = 0\right)$
$\frac{\partial h}{\partial x} = -\frac{1}{\epsilon} \cdot C = 0$
0
9
10
11
30
X

Figure 3. Boundary Conditions For Contaminant Transport In Porous Media.

RESULTS AND DISCUSSIONS

Results are obtained with the mesh arrangement shown in Figure 2 for d = 1, 10 and 20. The investigation is carried out utilizing a time step, t = 0.32 and a total of 20 time increments are given in each case. A visual representation describing the spread of the pollutants in the aquifer for d = 10 is presented in Figure 4 in the form of concentration isopleths plotted at the fifth and tenth time steps for a dispersivity of 0.05. It is also observed that as the dispersivity decreases or the inverse of the undisturbed hydraulic gradient increases the solutions tend to become unstable. It is also found that there is some change in concentration distribution if refined instead of coarse mesh is used.

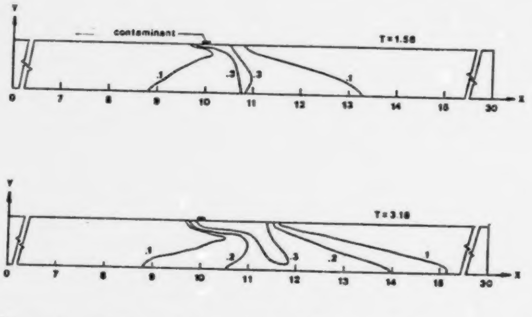

Figure 4. Concentration Contours For d=10 and ε=0.05.

CONCLUSION

Galerkin finite element method is seen versatile in solving flow problem in porous media. The mathematical model formulated in terms of a flow equation and a transient transport equation, coupled by the velocity and density terms predicts the spread of pollutants in time and space. The location and shapes of the concentration contours are significantly affected by the depth of aquifer and the Dispersion Coefficient. Stable solutions are obtained by utilizing a refined mesh near the pollutant source. For situations that warrant a high degree of accuracy, a refined mesh near the contaminant source is recommended.

ACKNOWLEDGEMENT

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GROUNDWATER POLLUTION IN NORTHWEST ARKANSAS

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ABSTRACT

Radar imagery photographs of Northwest Arkansas revealed that the near surface formations are heavily fractured with the fracture traces, or linears, easily traceable on the photographs. A superimposition of the linear traces on well and spring locations reveals that the springs and most higher producing wells are on these linears.

Since the linears provide an easy path for surface contaminants to enter these well and springs, it was reasoned that most would be contaminated. An investigation of 70 wells in an area 10 miles by 10 miles revealed that 80 percent were contaminated with coliform bacteria. Enumeration of aerogenes, fecal coliform and fecal Streptococci found a range of 1 to 2,080,000 organisms per 100 milliliters. A correlation was determined between high nitrate and high phosphate with the heavier concentration of bacteria. Sources of the contaminants were determined to be septic tank leach fields, confined live stock feeding, solid waste disposal landfills and spreading of agricultural wastes on pastureland.

Possibilities or corrective action are: reduced spreading of manu[illegible] on fields and pastures, better design of septic tank absorption fiel[illegible] on-site chlorinators for domestic water supplies and in some ca[illegible], extension of treated water supplies to rural areas.

These same conditions of shallow well contamination in fractured limestone probably exists in western Arkansas, eastern Oklahoma, southern Missouri and south-east Kansas.

A major environmental problem facing rural populations in carbonate (limestone and dolomite) areas is related to the development of safe and adequate supplies of groundwater. Carbonate terrains usually contain groundwater in solution channels developed along fracture zones. Water wells drilled to intercept these solution channels are more likely to have relatively high yields than wells drilled away from the channels. Unfortunately, these wells are also much more susceptible to pollution than wells not near a solution channel. The relationship between fractures and wells is shown in Figure 1. Water may move quite rapidly through such permeable zones in carbonate aquifers without natural filtering. Thus contamination can be a serious problem.

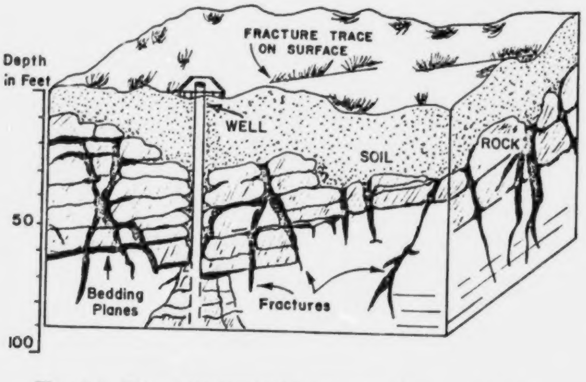

Figure I. The Relationship between Fractures and Wells

Much of the Ozarks Region (approximately 50,000 square miles in Arkansas, Oklahoma, Missouri, and Kansas) is underlain by carbonate rocks. Most shallow water wells and springs in Northwest Arkansas occur in carbonate rock. Radar imagery photographs show that most springs and the higher yielding wells are related to fractures in this carbonate rock.

The study area for this investigation lies in the extreme northern part of central Washington County, Arkansas. Its eastern boundary is 94°07'30 west longitude and the northern boundary in the Washington-Benton County line. The total area was 10 miles by 10 miles encompassing 100 square miles. The selection of this area was made because (1) a relatively large amount of geologic and soil data were readily available (2) the area is readily accessible, and (3) the site is representative of the carbonate terrain of the Ozark Mountains.

An example of the mapping of the surface fracture patterns is shown in Figure 2. This mapping may be accomplished by the interpretation of aerial photographs, to locate the surface expression of subsurface fracture zones. These linear features are natural in origin and may be soil tonal alignments; vegetation tone, type, or size alignments are topographic features such as straight stream segments or straight valley sections.

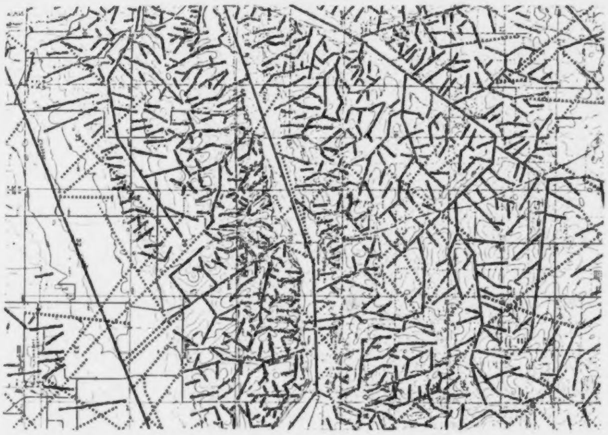

Figure 2. Example of Surface Fracture Patterns

Combinations of these types of expression are also possible. Springs and water wells were then selected as sampling sites on the basis of being either on or off the mapped linears. A remarkable correlation between springs and surface linear trends can be determined from topographic maps and aerial photos. The conclusion is that such linears indicate zones (fracture trends) of increased groundwater movement.

A bacteriological survey was conducted on 70 sites (11 springs and 59 wells). Approximately 80 percent of the water sources were bacteriologically polluted as shown in Table 1, with the water being unsafe for human consumption. Other analyses for heavy metals, nitrates and phosphates were also made with the result that most sites were below accepted levels for these materials with the exception of high nitrate concentrations in some of the sites with very high bacteriological concentrations.

Table 1. Results of Bacteriological Survey

Site number	Indication of surface contamination					Fecal contamination			
	None	Slight	Heavy	C[1]	S[2]	C	S	C	S
	Bacteria per 100 ml								
1	--	97	--	0		--		--	
2	--	23	--	0		--		--	
3	NS[3]	--	--	--		--		--	
4	--	175	--	0		--		--	
5	--	--	21,200	--		--		10	170
6	0	--	--	0		--		--	
7Sp[4]	--	--	7,200	--		--		544	635
8	--	11	--	0		--		--	
9	0	--	--	0		--		--	
10	0	--	--	0		--		--	
11Sp	--	--	2,500	--		--		112	169
12	1	--	--	0		--		--	
13	--	123	--	--		3	4	--	
14	--	9	--	0		--		--	
15	NS	--	--	--		--		--	
16	NS	--	--	--		--		--	
17	--	3	--	0		--		--	
18	--	53	--	--		4	4	--	
19	--	--	15,100	--		4	23	--	
20	--	--	3,805	--		5	2	--	
21	--	--	345	--		11	22	--	
22	NS	--	--	--		--		--	
23	--	--	2,975	0	1	--		--	
24	--	--	220	--		--		0	162
25	NS	--	--	--		--		--	
26	--	28	--	0	2	--		--	
27	--	85	--	0		--		--	
28	--	--	426	--		4	6	--	
29	NS	--	--	--		--		--	
30	NS	--	--	--		--		--	
31	--	--	4,555	--		3	60	--	
32	--	17	--	0		--		--	
33	--	24	--	0		--		--	
34	--	5	--	0		--		--	
35	0	--	--	0		--		--	
36	--	11	--	1	0	--		--	
37	--	--	492	--		0	26	--	
38	--	--	2,300	--		10	19	--	
39	--	8	--	0		--		--	
40	--	--	510	--		10	316	--	
41	0	--	--	0		--		--	
42	NS	--	--	--		--		--	
43	--	--	845	--		0	11	--	
44	0	--	--	0		--		--	
45	--	80	--	0		--		--	
46	--	--	325	--		--		78	434
47	--	--	780,000	--		--		139,000	102,500
48	--	--	--	--		--		1,960	7,500
49	--	165	--	0		--		--	
50	--	--	6,600	--		3	10	--	
51	--	--	214	--		5	113	--	
52	--	--	336	--		2	1	--	
53	0	--	--	--		2	455	--	
54	--	87	--	0	2	--		--	
55	0	--	--	0		--		--	
56	--	--	2080,000	0		--		--	
57	NS	--	--	--		--		--	
58Sp	--	--	970	--		1	157	--	
59SP	--	--	1,800	0		--		--	
60SP	--	--	136	--		8	9	--	
61SP	--	43	--	--		3	1	--	
62	--	14	--	0		--		--	
63Sp	--	--	57,933	--		--		626	212
64	--	--	17,600	--		--		17,600	1,300
65SP	--	--	14,900	--		3	57	--	
66	--	128	--	--		2	0	--	
67	0	--	--	0		--		--	
68	--	--	210	--		--		--	
69Sp	--	118	--	--		0	7	--	
70Sp	--	--	910	--		0	55	--	

[1] Coliform [2] Streptococci [3] Not sampled [4] Spring

CONCLUSIONS

Groundwater in the study area is dangerously polluted by bacteria. This pollution results from surface activities such as septic tank leach fields, animal wastes being applied to surface sites and other similar activity. Water supply wells should be tightly cased to depths below the surface linears, which in some cases extends to depths approaching 300 feet. Geologic design criteria for selection of sites for septic tank leach fields, sanitary landfills, and other surface activity that may contaminate groundwater should be established.

PHYSICAL TRANSPORT PROCESS FOR HYDROCARBONS IN THE SUBSURFACE

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ABSTRACT

The transport of hydrocarbons in the subsurface is a very complex combination of physical, chemical, and biological processes. While the chemical and biological processes are very important in the long-term transport of hydrocarbons, the short-term transport of hydrocarbons is dominated by the physical process. An understanding of the physical transport process will allow more efficient recovery of the hydrocarbon, leaving less in the subsurface to be acted upon by the chemical and biological processes.

This paper examines the physical process which controls the rate and extent of movement of hydrocarbons in the subsurface. The physical process of transport is dependent upon such factors as hydrocarbon viscosity, hydrocarbon density, hydrocarbon release rate, the hydrocarbon release volume, the water table depth, the groundwater gradient, water table fluctuation, subsoil grain size, and rainfall pattern. These factors are examined, and their impacts on rate and extent of hydrocarbon movement are addressed.

INTRODUCTION

The contamination of ground water by hydrocarbons is a problem of growing importance as more hydrocarbons are stored in more locations and the dependence on ground-water supplies increases with population growth and migration to areas dependent on ground water.

A particularly notable case of ground-water contamination came to light recently. The owner of Well A complained of an odd taste and smell in the water and was advised by the water well driller to chlorinate it. The taste and smell persisted. One evening, the well owner stepped into the bathtub shower, turned on the water and was scalded by pure hydrocarbon. It seems that the hydrocarbon was first detected in Well B, a well upgradient from the presently contaminated Well A, some 18 years ago. At that time the owner of Well B conducted an investigation, discovered a pipelike leak, repaired the leak and pumped fluid from Well B until it had cleared up. Well A did not exist at that time. The aquifer was essentially a sand.

Another notable case of ground-water contamination also developed recently. A fiberglass storage tank containing super unleaded gasoline ruptured, releasing 11,148 gallons into a limestone aquifer. A well located 380 feet from the tank had a hydrocarbon smell within 89 days after the rupture. Another well located 1,120 feet away had 0.8/feet of hydrocarbon within 91 days after the rupture.

These two cases suggest the wide range of environments in which contamination of a ground-water aquifer might occur. The rate at which the hydrocarbon transports and the extent to which it spreads is dependent on numerous factors, the most important of which are:

- Hydrocarbon viscosity,
- Hydrocarbon density,
- Hydrocarbon release rate,
- Hydrocarbon release volume,
- Ground-water gradient,
- Water table depth,
- Water table fluctuations,
- Subsoil pore size distribution, and
- Rainfall.

A reliable theoretical treatment of the hydrocarbon transport process is that of J. van Dam (1967). Mr. van Dam treats the transport process as a three-phase flow system utilizing saturation-dependent relative permeabilities. Capillary pressures are considered by Mr. van Dam because they are generally predominant forces in the case of hydrocarbon flow in a waterbearing stratum. The following discussions of infiltration and lateral migration draw heavily from van Dam's work.

HYDROCARBON INFILTRATION

Hydrocarbon infiltration may be conceptually described as fast or slow. Fast infiltration is defined here as a rate that will result in a mound of hydrocarbon at the water table sufficient in height to depress the water table. Slow infiltration is defined as a rate that will result in no mound or a mound of hydrocarbon insufficient in height to depress the water table. The process of hydrocarbon transport proceeds as follows for slow infiltration:

1. Hydrocarbon release is started.
2. Hydrocarbon flows downward under the influence of gravity.
3. Hydrocarbon fills the pores of the subsoil to an oil saturation sufficient to increase relative oil permeability to a magnitude great enough to handle the hydrocarbon flow rate but not more than 100% saturation minus the residual saturation of water and air.
4. Hydrocarbon migrates laterally as well as vertically under a saturation gradient which is also related to capillary forces at the hydrocarbon wetting front.

5a. Hydrocarbon release is stopped before a volume of hydrocarbon sufficient to reach the top of the water-air capillary fringe has been released.
5b. Hydrocarbon release is stopped before a volume of hydrocarbon sufficient to reach the bottom of the water-air capillary fringe has been released.
6a. Ambient air fills the pores of the subsoil to an air saturation equal to 100% saturation minus the residual saturation of water and hydrocarbon.
6b. Above the top of the former water-air capillary fringe, air fills the pores of the subsoil to an air saturation equal to 100% saturation minus the residual saturation of water and hydrocarbon. Within the former capillary fringe, the hydrocarbon moves laterally as the ambient air replaces the hydrocarbons. Lateral thinning of the hydrocarbon will continue until the hydrocarbon is everywhere at residual saturation.

The process of hydrocarbon transport for fast infiltration proceeds as for slow infiltration through step 4. The process then proceeds as follows:

5c. Hydrocarbon release is stopped after a volume of hydrocarbon sufficient to reach below the bottom of the former water-air capillary fringe (water table) has been released.
6c. Above the top of the former water-air capillary fringe, ambient air fills the pores of the subsoil to an air saturation equal to 100% saturation minus the residual saturation of water and hydrocarbon as hydrocarbon flows downward or laterally. Within the former capillary fringe, the hydrocarbon flows downward or laterally as the ambient air replaces the hydrocarbon. Below the bottom of the former water-air capillary fringe (water table), the hydrocarbon flows upward or laterally. The water is at residual saturation and remains immobile. Between the above layer where only residual water is present and the zone of the free ground water, which is 100% water-saturated, is an oil-water capillary zone. In this zone, water is above the residual saturation, and oil ranges from below to above residual saturation. Water and oil both

flow upward as long as they remain above residual saturation.

In the zone of free ground water, water moves upward to replace water and oil in the overlying layer.

LATERAL MIGRATION

The lateral transport of hydrocarbon on a horizontal water table proceeds as the mound of hydrocarbon approaches residual hydrocarbon saturation below the water table by flowing hydrocarbon laterally into a zone in the top of the water-air capillary zone. Lateral migration ceases when the hydrocarbon is everywhere at residual saturation. The area over which the hydrocarbon will spread at equilibrium may be estimated by the product of the leaked volume of hydrocarbon, the density difference between the hydrocarbon and water, the acceleration of gravity and the square root of Darcy permeability divided by the product of the air/oil wetability constant, the air/oil surface tension, residual oil saturation, and the 3/2 power of porosity.

An inclined water table tends to increase the rate and extent of migration in the direction of the inclination. The total area over which the hydrocarbon will spread at equilibrium when projected onto the horizontal plane is the same as for a horizontal water table.

DISCUSSION

The hydrocarbon viscosity and density influence both the flow rate and the extent of migration. Increasing density or decreasing viscosity increase the flow rate in direction proportion. The extent of migration is only indirectly impacted by viscosity. Increasing viscosity is associated with increasing residual saturation for hydrocarbons. Higher density tends to cause more depression of the water table or capillary fringe and therefore more loss of hydrocarbon to residual saturations. This leaves less hydrocarbon available to spread laterally.

The hydrocarbon release rate influences both the flow rate and the extent of migration. Higher release rates build higher mounds and therefore cause laterial flow rates to be higher. High release rates also depress the water table more and thereby lose some hydrocarbon to residual saturation in the mound which is not available to spread laterally.

The hydrocarbon release volume influences the extent of migration. Increasing the hydrocarbon release volume increases the area of migration in direct proportion.

Ground-water gradient influences both the flow rate and the extent of migration. Increasing the gradient increases the flow rate and the extent of migration. The extent of migration, as measured by the distance from the center of the infiltration area to the downgradient edge of the hydrocarbons, increases with the increase in ground-water gradient.

Water table depth influences the extent of migration. Increasing the water table depth decreases the extent of migration and the lateral flow rate. The extent of migration is reduced by typing up more hydrocarbon at residual saturation in the overlying soil.

Water table fluctuations influence the extent of migration. The total volume of sediments to which the hydrocarbons are exposed is increased by water table fluctuations. The more fluctuations which occur, the greater the magnitude of the fluctuations, and the longer the period of time over which they occur, the smaller the extent of migration.

Subsoil pore size distribution affects both the flow rate and the extent of migration. A pore size distribution which is associated with lower permeabilities (e.g. clays) would indicate lower flow rates. The same pore size distribution would tend to be associated with a higher porosity which would indicate a smaller extent of migration. Of course, a pore size distribution would tend to be associated with a higher permeabilities (e.g. sands) lower which would indicate higher flow rates and greater extent of migration.

Rainfall tends to have no effect on the flow rate or the extent of migration of the hydrocarbon except as it may influence other factors such as ground-water gradient, water table depth or water table fluctuations. Hydrocarbon does not appear to be "flushed out" by rainfall. The hydrocarbon tends to remain at residual saturation. However, there is evidence that the water soluble fraction of hydrocarbons would be relatively rapidly transported by percolating water (van der Waarden, et al, 1971).

CONCLUSION

The model of van Dam provides a strong framework for an understanding of transport process for hydrocarbons in the subsurface. A conceptual understanding of the physical transport process is an essential tool in the efficient investigation of ground-water contamination by hydrocarbons.

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DELINEATING GROUNDWATER CONTAMINATION BY HOUSEHOLD WASTEWATER

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ABSTRACT

A laboratory investigation and a confirming field study has been completed whereby groundwater contaminated by inadequately treated septic tank effluent can be easily delineated from other contaminating sources. The methodology involves fluorescent whitening agents (FWA) contained in commercial household laundry products found in virtually all household wastewaters; most domestic wastewater has between 0.2 and 0.4 mg/FWA.

A laboratory study of leachate from eight unsaturated 4 inch diameter soil columns treating septic tank effluents demonstrated a good correlation between FWA concentration and leachate water quality.

Leachate from lysimeters in two different existing septic tank leachfields were analyzed confirming the relationship between FWA concentrations and the septic tank leachfield water quality. No FWA was detected in well purified leachate but levels as high as 0.05 mg/l were found in leachates with high total organic carbon and high total coliform bacteria concentrations. Several contaminated wells and springs were examined, some with as much as 80 fecal coliform bacteria per 100 ml and total organic carbon in excess of 100 mg/l found free of FWA indicating agricultural or commercial sources not household wastewater. Others similarly contaminated did contain FWA indicating faulty septic tank systems as the sources.

INTRODUCTION

Ammonia, nitrates, chlorides, phosphates, total dissolved solids, total organic carbon, BOD, COD, and the coliform test have all been used to characterize groundwater quality. However, these constituents can originate from either human or animal sources. Separating these contaminates from either a human or an animal source is next to impossible without a long and lengthy study of the contaminated area. Clearly a constituent unique to either domestic wastewater or to animal wastes is needed if these two sources are to be delineated.

Many laundry detergents do have a component in their formulation which is not readily biodegradable. Typically laundry detergents contain about 0.5 percent fluorescent whitening agents, FWA, often referred to as brighteners or whiteners. Most household wastewaters have between 0.2 and 0.4 mg/l FWA. The presence of FWA in polluted groundwater is a definite indication of a household wastewater as the source.

PURPOSE AND SCOPE

The purpose of this research project was to develop a method differentiating the source of groundwater contamination between household wastewater and agricultural practices. The developed methodology involves detecting the presence of fluorescent whitening agents contained in commercial household laundry and cleaning products.

A laboratory investigation was carried out by applying septic tank effluent to soil and sand columns of varying depths. The column effluent was analyzed using the fluorescent whitening agent detection technique to determine if the technique could detect the presence of fluorescent whitening agents after the septic tank effluent received varying degrees of treatment.

Two confirming field studies were performed. First, samples collected from existing septic tank leachfields were analyzed for FWA presence. Second, springs and well water located in Northwest Arkansas known to be contaminated were examined.

DEVELOPING THE FWA DETENTION TECHNIQUE

To use a fluorescence technique to determine the presence of FWA standards were first developed. Personal communications with two detergent manufactures established that Tinopal Ames Pure and Tinopal 5BM were the most common FWA's incorporated into home laundry products. A review of literature demonstrated DASC-3 (Tinopal Ames Pure) and DASC-4 (Tinopal 5BM) as the most common FWA's found in the influent of wastewater treatment plants studied by Ganz (1975). Samples of these two FWA's were obtained to be used as standards.

To detect FWA in wastewater a modification of the organic extraction procedure employed by Uchiyama (1979) was developed because other organic matter may also fluoresce at the same wavelength as the FWA. Laboratory analyses found that as little as 1 mg/l FWA could be detected fluoremetrically in wastewater using 365 mm excitation and 430 mm emission wavelengths and 1,2 dichloroethane as the extraction solvent.

LABORATORY STUDY

Once each week the effluent from a four member family's septic tank was pumped into two five gallon plastic jugs and transported back to the laboratory. One of the jugs was stored in a refrigerator and used later in the week. The septic tank effluent was pumped from the remaining five gallon jug at a rate of 0.7 milliliters per minute using a Harvard Apparatus perstaltic.

Sand or soil was placed in 4 inch diameter ASTM D2729 PVC pipes, with stainless steel window screen placed over the bottom to help hold the material in the column, three inches at a time; the 3 inch layers were then lightly tamped ten times. Eight columns were constructed, four sand columns 3, 6, 12, and 24 inches deep and four soil columns of identical depths. Effluent from each column was funneled into 1 liter glass jars placed under each column.

The results are shown in TABLE I. TOC varied with depth going

TABLE I

COLUMN EFFLUENT CHARACTERISTICS
DURING LAST MONTH OF SAMPLING

SAMPLE	AVERAGE EFFLUENT TOC (mg/l)	AVERAGE EFFLUENT FWA (mg/l)
Septic Tank Eff.	101	0.44
3" soil	47	0.045
6" soil	49	0.007
12" soil	34	0.003
24" soil	35	N. D.*
3" sand	15	0.005
6" sand	13	N. D.
12" sand	12	N. D.
24" sand	12	N. D.*

* None Detected

from 47 mg/l for the 3 inch soil column down to less than 12 mg/l for the 24 inch sand column. Notice also that as the effluent TOC diminished, indicating better treatment, the concentration of FWA also decreases. Thus, properly treated septic tank effluent would not be expected to show FWA in the groundwater below the leachfield.

FIELD CONFIRMATION

The first field confirmation was conducted at the site of the septic tank effluent source, a farm household near the community of Savoy, Arkansas.

The first leachfield is labeled 01ST76 and is fed by gravity flow with the seepage bed situated 76-cm below the ground surface. The second leachfield studies is called 02MG30 and is also fed by gravity flow, but the seepage bed is located only 20-cm below the ground surface. Both systems are located in Nixa soils which are typically cherty silt loams exhibiting a very slow permeability. Samples drawn from monitoring wells situated around each system using a vacuum pump, were placed on ice and transported to the laboratory for FWA analyses.

The results are shown in Figure 1 for 01ST76, of the 10 sampling wells only five contained detectable levels of FWA. Two of these five wells, 1C1 and 1D1 are located in the bottom of the leaching bed and would be expected to have FWA. The other three wells are out from the bed and have received some soil treatment. Similarly, Figure 2 shows the results of the six wells sampled in system 02MG30. Only three wells were found to contain FWA. These results indicate that FWA may persist in water percolating through soil. Hence, confirming that poor septic tank treatment may show up as detectable levels of FWA in the groundwater.

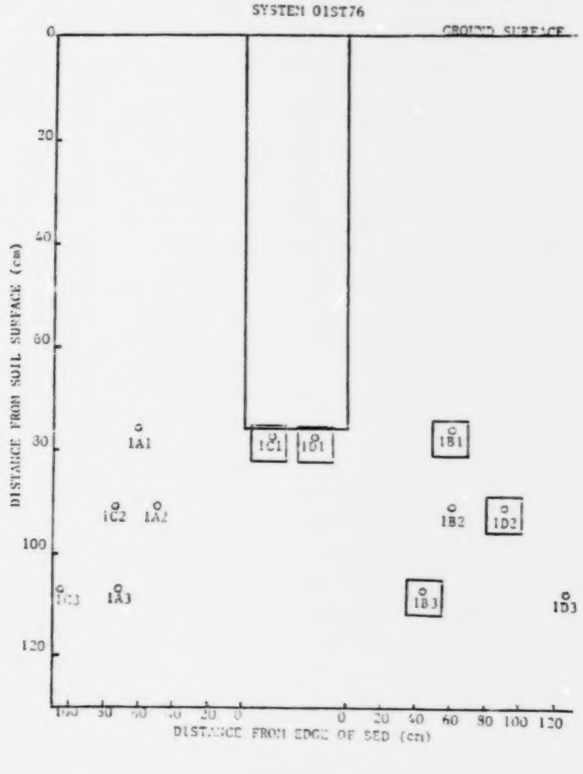

Figure 1: Sampling Wells from System 01ST76 Containing FWA's

The second confirming field study was from 12 wells and springs located in Northwest Arkansas. Several of these waters are used by local people as drinking water. A brief description of each sampling site follows:

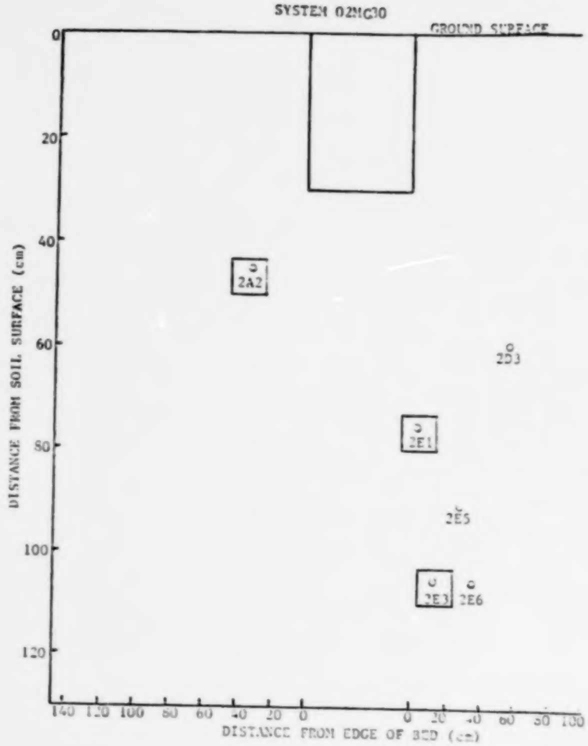

Figure 2: Sampling Wells from System 02MG30 Containing FWA's

Site 1: a spring almost 3/4 of a mile south of Eureka Springs, Arkansas.
Site 2: a spring almost 2 miles south of Eureka Springs, Arkansas.
Site 3: a spring surfacing in a ravine approximately 1 mile southeast of Eureka Springs.
Site 4: a spring located in the city of Eureka Springs.
Site 5: a spring surfacing in downtown Eureka Springs and the sample from this site was obtained in an underground pool in a cave.
Site 6: also a spring surfacing in downtown Eureka Springs.
Site 7: a spring in a ravine approximately 1 mile southeast of Eureka Springs.
Site 8: a spring located 3/4 mile south of Eureka Springs.
Site 9: a spring located in a small cave south of Eureka Springs.
Site 10: a spring 2 1/2 miles from Eureka Springs.
Site 11: a well located in the town of Hindsville, Arkansas. The well is situated in the center of a small commercial district.
Site 12: a small spring surfacing in a culvert approximately 2 miles southeast of Hindsville.

The results from chemical analyses and bacteriological examinations of the wells and springs are presented in TABLE II. The presence of FWA's in each sample is indicated by a yes for a positive identification and a no for a negative identification.

Many of the springs selected for study were found to be polluted during a study conducted in 1981, and it was believed wastewater exfiltration from the sewer system in the town of Eureka Springs was the source of much of the contamination. However, direct contamination by wastewater exfiltration was only identified in a couple of

TABLE II

Results of Field Tests on Spring and Well Samples

Site No.	Total Organic Carbon (mg/l)	Ammonia Nitrogen (mg/l)	Nitrate Nitrogen (mg/l)	Bacteria per 100 mills Total Coliform	Bacteria per 100 mills Fecal Coliform	Indicated Presence of FWA's
1	10	0.1	4.0	TNTC*	93	NO
2	10	1.0	4.5	280	110	NO
3	14	0.6	3.0	7	4	NO
4	11	0.1	2.5	11	26	YES
5	11	0.2	5.0	10	36	YES
6	12	0.2	7.5	36	5	NO
7	14	3.6	5.5	TNTC	88	NO
8	128	0.1	3.0	25	48	NO
9	24	0.2	5.0	150	98	YES
10	14	3.6	2.0	TNTC	TNTC	NO
11	11	0.5	15.0	178	82	NO
12	6	3.0	6.0	42	0	NO

*Too Numerous To Count

the springs when dye injected into the sewer system was detected in the springs. Most of the springs were simply classified as polluted with the source of contamination remaining unknown.

CONCLUSIONS

Based upon the results and discussions presented in this study, the following conclusions are drawn:

1. Fluorescent whitening agents may be used to augment the information required to determine the source of groundwater pollution.
2. High fluorescent whitening agents in groundwaters probably indicate household wastewater contamination.
3. Well treated household septic tank leachate will not contain marked concentrations of fluorescent whitening agents.

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VIRAL AND BACTERIAL CONTAMINATION OF GROUNDWATER BY ON-SITE WASTEWATER TREATMENT SYSTEMS IN SANDY COASTAL SOILS

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ABSTRACT

Contamination of groundwater by enteric viral and bacterial pathogens is an important public health concern for on-site wastewater treatment systems, especially in highly developed and populated coastal areas with permeable soils and seasonally high water tables. Viral and bacterial contamination of groundwater by on-site wastewater treatment systems was studied in an experimental field site on the N.C. coast. A low pressure dosing system applied septic tank effluent (STE) at three hydraulic loading rates to two, adjacent drainfields with the same sandy soil but different water table depths. In seasonal experiments known amounts of bovine enterovirus type 1 (BE-1) were added to the STE. Groundwater samples from the fields were analyzed for BE-1 twice weekly before, during and after virus dosing periods of three weeks. Fecal coliforms, fecal streptococci, coliphages and several chemical constituents were also measured periodically. Concentrations of BE-1, coliphages, fecal coliforms and fecal streptococci were reduced from their levels in STE in both fields; however, reductions were several $\log_{10}$ greater in the field with the deeper water table. BE-1 was detected in groundwater by the second day of virus dosing and persisted as long as 30 days post-dosing. There was no consistent pattern of increased microbial concentrations in groundwater at greater hydraulic loading rates of STE. Seasonal experiments showed temperature and overload effects on the system. The results demonstrate the importance of unsaturated flow for efficient removal of enteric viruses and bacteria by septic systems.

INTRODUCTION

The persistence, movement and fate of enteric viruses and other microbial pathogens is an important public health consideration in the siting, design and use of on-site wastewater treatment systems. Many of the factors that may influence the movement and survival of microbial pathogens in septic systems for wastewater have been identified from both laboratory and pilot scale field studies (Bitton, 1980; Duboise et al., 1979; Gerba et al., 1975; Kreissl, 1981; Sobsey, 1981). However, the impact of on-site wastewater treatment systems on groundwater quality in sandy coastal areas has not been adequately studied with respect to microbial contamination under controlled field conditions. This study examines how environmental and design factors of an experimental septic tank-soil absorption field system influence the persistence, movement and fate of a model enteric virus, bovine enterovirus type 1 (BE-1). The specific objectives of this study are: to determine how environmental factors (e.g. water table depth and seasonal variation in temperature and rainfall) and design factors (e.g. hydraulic loading rate, low pressure dosing and shallow trenches) influence the persistence, movement and fate of the model virus; and (2) to compare the fate of several indigenous wastewater microorganisms with that of the model virus and evaluate their effectiveness as indicators of treatment efficiency and water quality.

MATERIALS AND METHODS

Field Site.

Two adjacent experimental absorption fields were installed in a Corolla fine sandy soil (Aquic Quartzipsamment) on a coastal barrier island in eastern North Carolina. The site is on a 1% slope, and in one field (high field) the seasonally high water table depth is 0.6 to 0.9 M, while in the other field (low field) it is 0.3 to 0.45 M. Each absorption field consisted of a series of 3 x 0.6 M trenches. Separate trenches were dosed with septic tank effluent (STE) at loading rates of 10, 40 or 160 L/M^2/day in order to model conservative, typical and overload rates, respectively.

Domestic wastewater pumped from nearby condominiums was treated in a series of three septic tanks. In order to achieve consistent loading rates, STE from the final tank was dosed at low pressure into the trenches twice daily by a timer-controlled pump.

Enteric Virus and Virus Assays.

Bovine enterovirus type 1 (BE-1) was pumped into the STE distribution lines during each dosing cycle for experimental periods of 30 days. Approximately 5 x 10^4 plaque-forming units (PFU) were added per liter of STE. All virus assays were done by the plaque technique in MA104 cell cultures. Neutralization tests with BE-1 antiserum were performed on viruses isolated from groundwater to confirm that they were the same viruses added to the STE.

Sampling and Analyses.

Groundwater samples were collected twice weekly from PVC monitoring wells (1.5 to 1.9 M deep) placed 0.3, 1.5 and 3 M downgradient from each trench. Samples were drawn from triplicate trenches for each loading rate. STE samples were taken from the distribution lines of each field during dosing cycles. Samples were collected fortnightly for analysis of $NH_4 - N$, $NO_3 - N$, soluble P, Na and K. Fecal coliforms (FC), fecal streptococci (FS) and coliphages (PH) were measured monthly. FC and FS were analyzed by MPN and MF procedures, respectively (APHA, 1980), and coliphages were assayed by conventional plague methods on *E. coli* C3000. Water table depths were monitored continuously by Stevens type F level recorders in each field.

BE-1 Concentration by $A1OH_3$ Precipitation.

STE and groundwater samples of 500 ml were adjusted to pH 6.0 and supplemented with $A1C1_3$to final concentrations of 0.00015 and 0.001 M, respectively. After stirring slowly for 15 min. to promote floc formation, samples were centrifuged at 1850 x g for 15 min. Viruses were eluted from the sedimented aluminum floc by resuspending in 4.5 ml of 3% beef extract (BE) and adjusting to pH 7.5. After centrifuging to sediment undissolved material, the virus-containing supernatant was collected. The sediment was further eluted with another 4.5 ml of BE, and the supernatant after centrifugation was combined with the first BE supernatant. These concentrates were stored at − 40°C for virus assay.

RESULTS AND DISCUSSION

The results of three seasonal experiments (winter, summer and fall) are summarized in Tables 1, 2 and 3, respectively. Low field performance is compared to that of the high field for the dosing and post-dosing periods separately as well as for both periods combined. The low field results for the winter experiment indicate relatively little reduction of BE-1 in groundwater compared to levels in the STE (Table 1). In all other seasonal experiments BE-1 concentrations in groundwaters of both fields were lower than those in STE.

TABLE 1. BE-1 CONCENTRATIONS[1] IN STE AND GROUNDWATER AND WATER TABLE DEPTH - WINTER EXPERIMENT

	Dosing[2]		Post-Dosing[3]		Combined	
			HIGH FIELD			
STE	2.6		0.71		1.6	
Loading Rate:						
10 L/M^2/day	0.60		0.52		0.55	
40 L/M^2/day	0.63		0.52		0.57	
160 L/M^2/day	0.72		0.52		0.61	
Water Table Depth (M)	0.755		0.780		0.769	
			LOW FIELD			
S.	2.0		0.81		1.4	
	0.3M[4]	1.5M[4]	0.3M	1.5M	0.3M	1.5M
10 L/M^2/day	3.3	2.7	2.5	2.0	2.8	2.3
40 L/M^2/day	3.5	2.2	2.3	1.6	2.8	1.9
160 L/M^2/day	3.6	2.6	2.6	2.2	3.0	2.4
Water Table Depth (M)	0.395		0.454		0.429	

1) Log$_{10}$ mean concentration PFU/L
2) Dosing Period = Day 1-22
3) Post-Dosing Period = Day 23-58
4) Distances of groundwater observation wells from trenches

SIGNIFICANT DIFFERENCES (p < 0.05 ÷ 3 < 0.017)

	H INP	HQ	H1	H4	L INP	LQ	L1	L4	LQ5	L15	L45
H INP		*	*	*							
HQ	*										
H1	*										
H4	*										
L INP						*	*	*			
LQ					*			*	*		
L1					*					*	
L4					*	*					*

H = High field; L = Low field; INP = Virus in STE;
Q = 10 L/M^2/day (groundwater); 1 = 40 L/M^2/day (groundwater);
4 = 160 L/M^2/day (groundwater); 5 = 1.5 M well from trench.

TABLE 2. BE-1 CONCENTRATIONS[1] IN STE AND GROUNDWATER AND WATER TABLE DEPTH - SUMMER EXPERIMENT

	Dosing[2]			Post-Dosing[3]			Combined		
				HIGH FIELD					
STE	2.4			0.80			2.2		
Loading Rate:									
10 L/M^2/day	0.78			0.81			0.74		
40 L/M^2/day	0.77			0.78			0.77		
160 L/M^2/day	0.78			0.76			0.78		
Water Table Depth (M)	1.16			0.24			0.17		
				LOW FIELD					
STE	2.0			0.81			1.4		
	0.3M[4]	1.5M[4]	3M[4]	0.3M	1.5M	3M	0.3M	1.5M	3M
10 L/M^2/day	1.5	1.5	0.80	0.75	0.80	-	1.3	1.3	0.80
40 L/M^2/day	1.2	1.2	0.79	0.78	0.78	-	1.1	1.1	0.79
160 L/M^2/day	1.5	1.1	0.84	0.79	0.78	-	1.3	1.0	0.84
Water Table Depth (M)	0.674			0.914			0.725		

1) Log$_{10}$ mean concentration PFU/L
2) Dosing Period = Day 1-22
3) Post-Dosing Period = Day 23-58
4) Distances of groundwater observation wells from trenches

SIGNIFICANT DIFFERENCES (p < 0.05 ÷ 3 < 0.017)

	H INP	HQ	H1	H4	L INP	LQ	L1
H INP		*	*	*			
HQ	*						
H1	*						
H4	*						
L INP							*

H = High field; L = Low field; INP = Virus in STE;
Q = 10 L/M^2/day (groundwater); 1 = 40 L/M^2/day (groundwater);
4 = 160 L/M^2/day (groundwater).

TABLE 3. BE-1 CONCENTRATIONS[1] IN STE AND GROUNDWATER AND WATER TABLE DEPTH - FALL EXPERIMENT

	Dosing[2]			Post-Dosing[3]			Combined		
				HIGH FIELD					
STE	2.4			0.96			1.7		
Loading Rate:									
10 L/M^2/day	0.83			0.74			0.79		
40 L/M^2/day	0.77			0.75			0.76		
160 L/M^2/day	0.80			0.77			0.78		
Water Table Depth (M)	1.00			1.01			1.01		
				LOW FIELD					
STE	2.7			1.1			2.0		
	0.3M[4]	1.5M[4]	3M[4]	0.3M	1.5M	3M	0.3M	1.5M	3M
10 L/M^2/day	1.1	0.75	0.75	0.80	0.74	0.73	0.94	0.75	0.74
40 L/M^2/day	1.8	0.75	0.81	0.88	0.75	0.72	1.3	0.75	0.76
160 L/M^2/day	0.86	0.76	0.75	0.76	0.75	0.75	0.81	0.75	0.75
Water Table Depth (M)	0.650			0.683			0.666		

1) Log$_{10}$ mean concentration PFU/L
2) Dosing Period = Day 1-22
3) Post-Dosing Period = Day 23-58
4) Distances of groundwater observation wells from trenches

SIGNIFICANT DIFFERENCES (p < 0.05 ÷ 3 < 0.017)

	H INP	HQ	H1	H4	L INP	LQ	L1
H INP		*	*	*			
HQ	*						
H1	*						
H4	*						
L INP					*	*	*

H = High field; L = Low field; INP = Virus in STE;
Q = 10 L/M^2/day (groundwater); 1 = 40 L/M^2/day (groundwater);
4 = 160 L/M^2/day (groundwater).

Water Table Depth.

Vertical distance of unsaturated flow to the water table was found to be the most important factor affecting virus levels in groundwater. This relationship was demonstrated by the dramatic difference between high field groundwater, from which BE-1 was rarely isolated, and low field groundwater, from which BE-1 was sometimes recovered at high concentrations. Seasonal variations in water table may be the major reason for the observed differences in virus recovery in winter, summer and fall experiments. BE-1 concentrations in groundwater were highest in the winter when the water table was nearest the surface (Table 1).

Persistence.

BE-1 was observed to persist and accumulate in groundwater, especially in the low field (Table 1). In the winter experiment BE-1 persisted as long as 30 days post-dosing. BE-1 also appeared to persist and accumulate in the soil because virus concentrations in groundwater increased dramatically after heavy rainfall.

Movement.

Horizontal movement of the virus was rapid when the water table was shallow. BE-1 was detected in groundwater by the second day of virus dosing. In the winter experiment the 0.3 M wells had significantly ($p<0.017$) higher concentrations of BE-1 than the 1.5 M wells (Table 1). In the summer experiment, when the water table was relatively deep, a ''wave'' effect was observed as the peak of virus concentration successively passed from the 0.3 M to the 1.5 and 3.0 M wells over time.

Hydraulic Loading.

Loading rate effects on virus levels in groundwater were not consistently observed. The effect of system overload was tested in the summer experiment by continuous dosing for several days. This resulted in increased BE-1 concentrations in groundwater despite a deep water table.

Indicator Organisms.

Table 4 compares the treatment efficiencies of the high and low field for several indigenous microorganisms, as well as for BE-1. The results for idigenous microorganisms are based on mean values from corresponding sampling dates throughout the study. All of the indigenous wastewater microorganisms measured were removed to a

TABLE 4. LOG$_{10}$ MEAN CONCENTRATIONS (I.U./L) OF FECAL COLIFORMS, COLIPHAGES, AND FECAL STREPTOCOCCI IN STE AND GROUNDWATER

Sample	Fecal Coliforms		Coliphages		Fecal Strep.	
STE	6.4		5.8		6.7	
			Low Field			
	0.3M[a]	1.5M[a]	0.3M	1.5M	0.3M	1.5M
Groundwater:						
10 L/M^2/day[b]	3.5	3.3	3.3	2.9	3.1	2.9
40 L/M^2/day	3.7	2.9	3.3	2.7	3.6	2.6
160 L/M^2/day	4.7	3.3	3.2	2.8	4.6	3.3
			High Field[c]			
Groundwater:						
10 L/M^2/day	2.2		2.2		1.1	
40 L/M^2/day	2.6		2.2		1.2	
160 L/M^2/day	2.5		2.2		1.4	

[a] Distances of groundwater observation wells from trenches.
[b] Hydraulic loading rates of trenches in absorption fields from which groundwater was collected.
[c] Groundwater observation wells were 0.3M from trenches.

greater extent than was BE-1. However, measurements of these indicator organisms confirmed the importance of vertical distance of unsaturated flow by demonstrating differences in their groundwater concentrations between low and high fields.

CONCLUSIONS

The results of this study suggest that careful consideration should be given to the use of septic tank-soil absorption systems in coastal areas having coarse soils and seasonally high water tables. Pressure for development has led to lenient vertical separation regulations in North Carolina and other coastal areas. The design conditions modeled in the low field of this study meet or exceed the legal requirements of many states. The implications of these findings are important for those coastal areas which depend on groundwater for their source of drinking water or for other beneficial purposes. The results of this study indicate that the use of septic tank-soil absorption systems in permeable soils with shallow water tables can contaminate groundwater supplies. Improved or alternative methods of wastewater treatment should be considered in order to protect groundwater resources of these areas.

ACKNOWLEDGMENTS

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NITRATE CONCENTRATIONS IN MUNICIPAL WELLS LOCATED WITHIN A RIVER BED

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INTRODUCTION

Municipalities in the Central Platte Valley of Nebraska utilize the alluvial aquifer of the Platte River for drinking water. Of concern to these municipalities is the potential for nitrate contamination of these well fields. Such contamination could result from periods of low-flow or no-flow in the River, in part caused by increased diversions of River waste for irrigation upstream. Drawdown in the well field during these periods could allow high nitrate groundwater (25 to 50 mg/l NO_3-N, Exner and Spalding, 1976), to the north of the River to flow into the alluvial well field. In order to manage the River and groundwater conjunctively for both quantity and quality, a management model is needed. This paper describes such a model. It utilizes the Theis non-equilibrium equation with a modified image method to calculate drawdown; it introduces the concept of a critical recharge rate to determine the conditions under which hydraulic connection between the river and groundwater is broken; and it uses a weighted average approach to evaluate the mix of nitrate concentrations that enter the well. It is distinctive in that it integrates models of drawdown and groundwater quality, evaluates recharge as a function of pumping rate as well as streambed permeability and river flow, and evaluates the nitrate concentration in the well as function of the amount of water entering the well from the river and from two aquifer zones.

Data for the Grand Island, Nebraska well field on Indian Island (Fig. 1) were used to develop the model. However, no field tests of aquifer response to varying flow conditions have been made and data on the thickness of each aquifer zone are unavailable. Thus, the model has not yet been validated. It has been tested using publishing data from field tests on other aquifer-stream systems. When validated it can be used to evaluate municipal well field management alternatives, to evaluate the impact on well field water quality of river diversions for new irrigation projects, and to determine the number of consecutive no-flow days that can be sustained without damaging well field water quality.

This paper describes the study area, summarizes the model conceptually and mathematically, and provides results for three simulations.

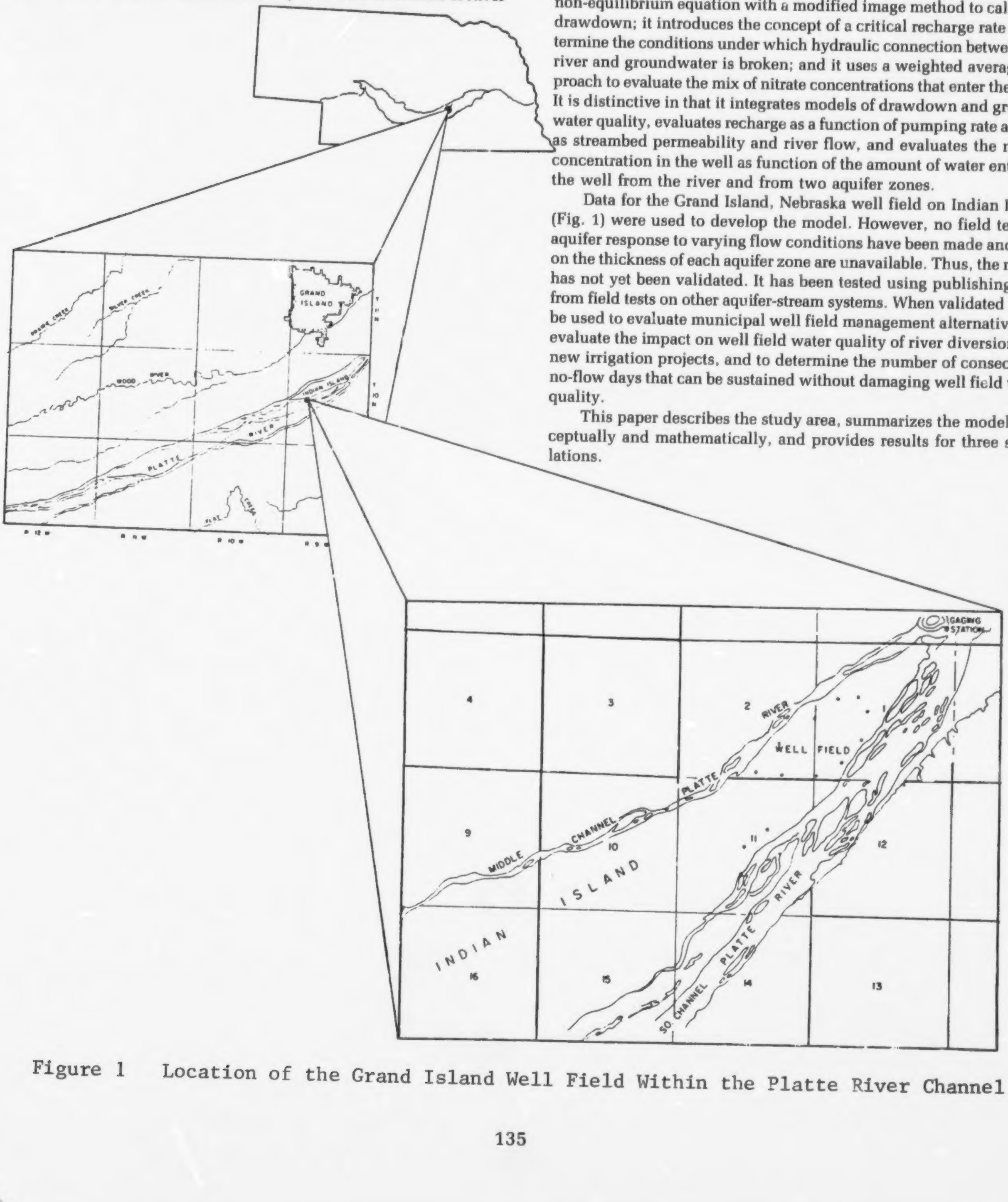

Figure 1 Location of the Grand Island Well Field Within the Platte River Channel

THE GRAND ISLAND WELL FIELD

Braiding of the Platte River channel in south central Nebraska creates numerous permanent islands within the channel (Fig. 1). The Grand Island well field is located on such an island about 6 miles long and 1 mile wide. The River is underlain by alluvial clay, silt, sand and gravel of Quarternary age deposited in a series of troughs within the underlying cretaceous shales and limestones. This alluvium contains the principal aquifer—about 150 feet of sand and gravel underlain by another 125 feet of clay or silt. The aquifer is in hydraulic connection with the Platte River when water is present in one or more of the channels. Historically, the River channels on either side of the island have been dry about 26 days per year, primarily during July, August and September.

Water table contours indicate that groundwater movement beneath the island is to the northeast, parallel to the principal direction of flow of the River. However, during periods of low flow when well field pumping continues, groundwater is expected to move from northwest to southeast into the well field. This groundwater is from agricultural areas and is, therefore, high in nitrate (25-50 mg/l NO_3-N). Data from a nearby island indicate that groundwater levels along the Platte River respond rapidly to changes in river stage, usually within 24 hours for distances up to 2500 feet from the edge of the River (Hurr, 1981).

There are 12 domestic wells on Indian Island; they average 48 inches in diameter and 130 feet deep (screened in the lower 80 feet); pumping rates are 1500 to 2000 gallons per minute in each well.

THE MODEL CONCEPTUALLY

This model makes the assumption that the well-field is in the center of the island. The aquifer is divided into two zones, an upper layer with high nitrate concentrations overlying a lower layer with lower nitrate concentrations. Conceptually, three types of calculations are involved and the model addresses them sequentially.

First, the recharge rate and drawdown around the well are evaluated, given a certain pumping rate. Figs. 2 and 3 show the flow lines to the well for the case in which hydraulic connection between the river and groundwater is maintained and for the case in which that hydraulic connection is broken. Like other models (DeVries, 1970), the Theis nonequilibrium equation is used with the image method. However, other models generally assume that the recharge rate into the image well is always equal to the pumping rate. Consequently, they do not account for the recharge capability of the river as measured by streambed permeability and/or river flow. In this model recharge is a function of pumping rate, streambed permeability, and river flow.

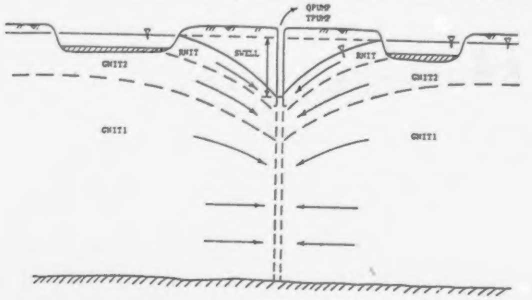

Fig. 2. Flow into the Well when Hydraulic Connection is Maintained

QPUMP= Pumping Rate
TPUMP= Pumping Time
RNIT= River Water Concentration
SWELL= Well Drawdown
GNIT2= Concentration of Aquifer Upper Zone
GNIT1= Concentration of Aquifer Lower Zone
QRECH= River Recharge RAte

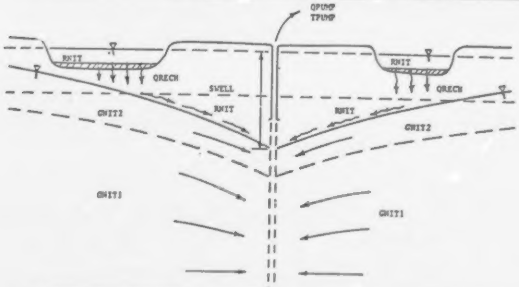

Fig. 3. Flow into the Well when Hydraulic Connection is Broken

Secondly, the nitrate concentration in the well is evaluated as a function of drawdown, depth to perforations, depth of the well, thickness of the aquifer zones with different nitrate concentrations, and the nitrate concentrations of those zones. Zone thicknesses at the well are first established, then the concentration is computed as the weighted average concentration of water entering the well from each zone. Figs. 4 and 5 illustrate the situation in which drawdown is such that the water level in the well falls below the well casing; hydraulic connection is maintained in one case (Fig. 4) and broken in another (Fig. 5). The approach is an extension of a model developed by Lyons (1976) for an aquifer that is stratified with respect to quality. However, Lyons assumes that the water in a well comes only from one aquifer zone; thus, this weighted average approach is unique.

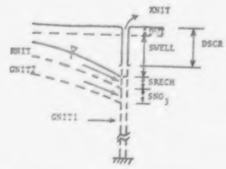

Fig. 4. Nitrate Concentration of the Well Water when the Water Level in the Well Falls below the Well Casing (Hydraulic Connection Maintained)

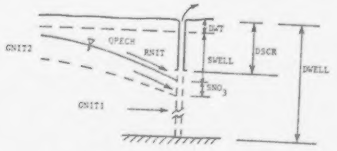

Fig. 5. Nitrate Concentration of Well Water When the Water Level in the Well Falls Below the Well Casing (Hydraulic Connection Broken)

RNIT	River Water Concentration
DWT	Depth to Water Table
DSCR	Depth to Perforations
SWELL	Well Drawdown
SRECH	Thickness of Recharge Water at the Well
SNO3	Thickness of Contaminated Layer at the Well
GNIT2	Concentration of Aquifer Upper Zone
GNIT1	Concentration of Aquifer Lower Zone
XNIT	Concentration in the Well Water
DWELL	Well Depth
QRECH	River Recharge Rate

Complicating the analysis is the fact that the effects of low river flow and/or high pumping rates do not appear in the well field instantaneously. Rather, there is a time lag, the magnitude of which is determined by the distance from the well field to the river, by the hydraulic conductivity of the aquifer, and by the hydraulic gradient into the well field (essentially the drawdown). Thus, the conditions which can cause a water quality problem must be sustained for some time period prior to the problem actually developing. The third type of calculation is aimed at determining this time lag. It is evaluated as the sum of the vertical travel time and the horizontal travel time, where the vertical travel time is zero for the case in which hydraulic conection is maintained. In both cases, expressions for vertical and horizontal velocity are derived from Darcy's law.

RESULTS

The system was simulated for a range of pumping rates under average flow and no-flow conditions. Input data are summarized in Table 1. For pumping rates between 500 and 2400 gallons per minute, drawdown ranges from 4.6 to 21.9 feet, the radius of influence ranges from 319 to 456 feet, and the nitrate concentration does not change. It remains 0.2 mg/l which is the input concentration for the lower layer

Table 1 Input Data For The System Simulation

Input Data	Code	Value or Range	Source
(1) River Characteristics			
• Width of left channel	W1	250 ft	USGS Map (1:24,000)
• Width of right channel	W2	2,100 ft	USGS Map (1:24,000)
• Depth of water in river	DRIVER	5-10 ft	Estimate
• NO_3 Concentration of river water	RNIT	0.0 - 1.3 ppm	USGS Water Supply Paper 2179
• Hydraulic Conductivity of river bed	KBED	20 gpd/ft^2	Estimate (From the Little Plover River Experiment Weeks, et.al.1965)
• Thickness of Semipervious layer of streambed	DBED	0.1 - 1.0 ft	Estimate
(2) Aquifer Characteristics			
• Depth to water table	DWT	3.0 - 6.0 ft	Registration records
• Depth of Polluted Upper Layer	DNO3	10.0 - 20.0 ft	Estimate
• NO_3 Concentration of upper layer	XNIT2	50.0 ppm	Estimate
• NO_3 Concentration of lower layer	XNIT1	0.0 - 0.2 ppm	Estimate(Utilities Dept., 198
• Transmissivity	T	119,375-126,000 gpd/ft	Compute from K and aquifer thickness
• Hydraulic conductivity	K	955-1,008 gpd/ft	Wenzel,1942
• Coefficient of storage	S	0.217	Wenzel, 1942
(3) Well Characteristics			
• Distance from well to river	XRIVER	1,500 ft	USGS map (1:24,000)
• Depth of well	DWELL	130 ft	Registration Record
• Radius of well	RWELL	2.0 ft	"
• Depth to perforations	DSCR	50 ft	"
• Pumping rate	QPUMP	1,500-2,100 gpm	"
• Pumping time	TPUMP	8 hrs	"

of the aquifer. Nitrate concentrations do not change because the drawdown is less than the depth to the screen for all pumping rates and all flow conditions. For a pumping range of 1500 to 2100 gpm, predicted drawdowns (13.7 to 19.2 feet) compare favorably with drawdowns measured during well testing (14.6 to 23.4 feet).

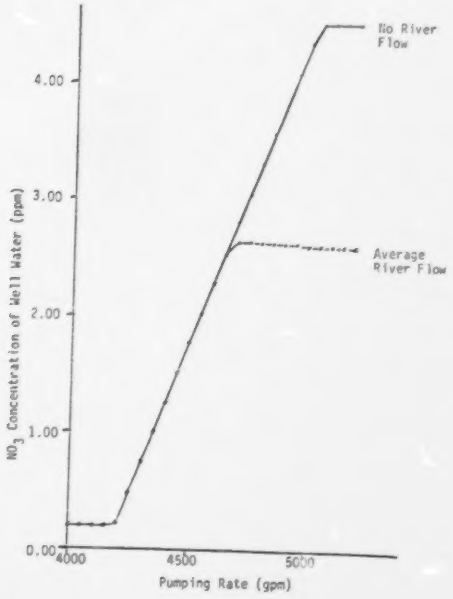

Fig. 6 Relationship Between NO_3 concentrations and Pumping Rates

Higher pumping rates, however, do cause water quality impacts. For pumping rates between 4100 and 5050 gpm and average flow as well as no-flow conditions, drawdown is 37.5 to 46.2 feet and the radius of influence is 504 to 518 feet. For pumping rates above 4150 gpm, the drawdown reaches the screen and low quality water begins to enter the well. For no-flow conditions in the river, the nitrate concentration increases steadily with an increase in pumping rates reaching a maximum value of 4.55 ppm at the rate of 5050 gpm (Fig. 6). For average flow conditions, the nitrate concentration reaches a maximum value of 2.47 gpm at a pumping rate of 4650 gpm and then decreases to 2.42 ppm (Fig. 6). This decrease is due to the diluting effect of river water. Hydraulic connection is maintained in all cases. Calculated lag times decrease with increasing pumping rates. Depending on the pumping rate, nitrate concentrations begin to increase for lag times between 292 and 342 days. They level off at their steady state values for lag times between 326 and 388 days.

In order to test the model further, published data from field tests on the Little Plover stream-aquifer system in Wisconsin were utilized in another simulation. The field tests had indicated a break in the hydraulic connection between the River and its alluvial aquifer. Using river and aquifer data for that system, this model also predicted a break in the hydraulic connection with predicted drawdowns at the River of 0.63 to 1.46 feet below the streambed. Measured data at one gaging station suggested a recharge rate of 404 gpm. The simulation predicted a recharge rate of 430 gpm, slightly higher than suggested by the measurements because the predicted zone of influence extends farther downstream than the gaging station.

DISCUSSION

A model that integrates drawdown and groundwater quality considerations in an alluvial aquifer has been developed for a municipal well field in central Nebraska. It is distinctive in that it considers streambed permeability and river flow as well as pumping rate in evaluating recharge, and it calculates nitrate concentrations as a function of the amount of water entering the well from several zones. While not validated with a field test, model predictions are reasonable and accurate to the extent they can be compared to measured data. Field tests are planned for the summer of 1984. When validated, the model may be used to evaluate the impact of diversions for irrigation upstream on well field quality.

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FINITE ANALYTIC METHOD FOR SOLUTION OF ONE-DIMENSIONAL TRANSIENT TRANSPORT EQUATIONS

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ABSTRACT

A new numerical method called finite analytic method is proposed to solve the ground water solute transport problems. This method differs from the others in that it incorporates local analytical solutions to a numerical scheme for the linear or nonlinear partial differential equation describing the global problem.

The proposed method is used to solve three cases of one-dimensional convective-dominated solute transport problems in ground water system. They are less, moderately and highly convective dominated transport problems with grid peclet number equals to 1, 10, and 100 respectively. The corresponding dispersion coefficients are 0.25, 0.025 and 0.0025 respectively. The other physical parameters considered for the solution scheme are seepage velocity of 0.5, spatial grid length of 0.5 and a time interval of 0.4. The results are compared with the exact solution, Crank-Nicholson finite difference scheme and Galerkin finite element method. The new scheme is capable of producing reliable and stable solutions.

INTRODUCTION

The one-dimensional convective transport equation has been widely used to describe approximately the transient motion of a subset of particles in porous media flow. Such a transport phenomenon, when considered for an ideal solute or tracer element (i.e., of constant density and viscosity) being present in a rigid isotropic porous medium saturated with an incompressible fluid (= water), may be represented by

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} - D\frac{\partial^2 c}{\partial x^2} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, c is solute concentration; u is seepage velocity; D is dispersion coefficient; x and t are the cartesian coordinate and time axes respectively.

The problem can be solved either by exact analytical methods or by some numerical methods, the most popular of which are the finite difference (FD) and finite element (FE) methods. However an alternate formulation of the problem is possible with the aid of analytical solution techniques like transformation of variables, separation of variables, principles of superposition, Duhamel's principle, etc. A new numerical method called the finite analytic (FA) method is presented here based on the above mentioned analytical solution techniques.

The FA method is based on incorporation of analytical solution to local elements or subregions of a flow field. The FA method has so far been applied to the cavity flow problems in heat transfer (Chen and Li, 1979, 1980; Chen, et al., 1981). The basic philosophy behind this method is to invoke analytic solution of governing partial differential equation (PDE) in numerical solution scheme of a problem, where the entire flow field is subdivided into a number of small subregions or local elements. The governing equation for the elements is linearized locally, if necessary, and then an analytical solution is sought for the subregions. The analytic solution for local elements is expressed in an algebraic form, relating an interior node of the subregion to its neighboring nodes. This results in a system of algebraic equations which is then solved to provide the numerical solution of the complete problem.

The purpose of this paper is to introduce the FA method to solve solute transport problems in ground water, demonstrate its application, and compare its results with the other existing numerical methods.

FORMULATION OF PROBLEM

Consider the finite analytic formulation of a one-dimensional problem as defined by equation (1). For computational convenience, all the variables are considered normalized so that they may be expressed in dimensionless form as

$$x = x/L; \; u = u/U; \; D = D/UL; \; t = tU/L$$

where, L and U are some normalizing factors of length and velocity respectively. The governing equation for each element describing the global problem may now be written as

$$c_{xx} = (2\alpha)c_x + (\theta)c_t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where, $2\alpha = u/D$; $\theta = 1/D$; and the subscripts denote the differentials. The relationship described above is now solved by the FA method following the steps sequentially as given below.

Step 1.

The field is discretized into a number of rectangular subregions as shown in Figure 1. Each local element shown in Figure 1 constitutes a subregion of $2\Delta x \times \Delta t$ ($= 2h \times k$). The analytic solution is sought for each point (i,j) represented by such an element and then assembled to represent the entire problem. Each point (i,j) is surrounded by five other neighboring points (i-l, j-l), (i-l,j), (i,j-l), (i+l, j-l) and (i+l,j). For notational convenience these six points are indexed as P, SW, WC, SC, SE and EC respectively representing the west (W), south (S) and east (E) boundaries of the element (see Figure 1).

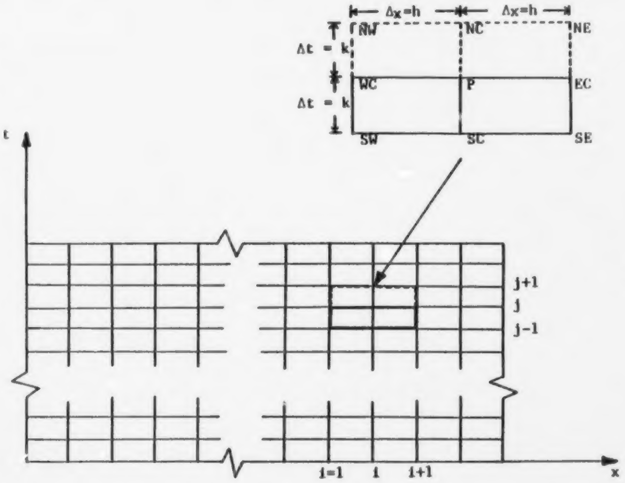

Figure 1. Domain and Element of FA Method.

Step 2.

The local element represented in Figure 1 does not have a north (N) boundary; the east and west boundaries are expressed as function of two nodal points; while, only the south boundary is defined by a three nodal points function. The initial and boundary conditions for the local element are prescribed in a polynomial form in terms of the available nodal values, such as

$$f_N(x) = 0 \quad \text{(3a)}$$

$$f_S(x) = c(x,0) = a_{0S} + a_{1S}x + a_{2S}x^2 \quad \text{(3b)}$$

$$f_E(t) = c(+h,t) = a_{0E} + a_{1E}t \quad \text{(3c)}$$

$$f_W(t) = c(-h,t) = a_{0W} + a_{1W}\,t \quad \text{(3d)}$$

where, $f(\cdot)$ represents the functional form, and

$$a_{0S} = c_{SC};\ a_{1S} = (c_{SE} - c_{SW})/(2h);$$

$$a_{2S} = (c_{SE} - 2c_{SC} + c_{SW})/(2h^2) \quad \text{(4a)}$$

$$a_{0E} = c_{SE};\ a_{1E} = (c_{EC} - c_{SE})/(k) \quad \text{(4b)}$$

$$a_{0W} = c_{SW};\ a_{1W} = (c_{WC} - c_{SW})/(k) \quad \text{(4c)}$$

and $h = \Delta x$, $k = \Delta t$

Step 3.

The problem at this stage is mathematically well defined by equations (2) thru (4). The analytic solution can be obtained by the method of separation of variables. The solution for each interior nodal point P in a local element results in a six point formula which may be given as

$$c_P = A_{WC}c_{WC} + A_{EC}c_{EC} + A_{SC}c_{SC} + A_{SW}c_{SW} + A_{SE}c_{SE} \quad \text{(5)}$$

where, the five analytic coefficients are

$$A_{WC} = [Q_1 - h^2\theta(Q_2-P_2)/k] \cdot \exp(\alpha h) \quad \text{(6a)}$$

$$A_{EC} = A_{WC} \cdot \exp(-2\alpha h) \quad \text{(6b)}$$

$$A_{SC} = [2P_2(1+2\alpha h) - 8P_3(\alpha h)^2] \cdot \exp(\alpha h)$$
$$+ [2P_2(1-2\alpha h) - 8P_3(\alpha h)^2] \cdot \exp(-\alpha h) \quad \text{(6c)}$$

$$A_{SW} = [-P_2(1+3\alpha h) + h^2\theta(Q_2-P_2)/k + 4P_3(\alpha h)^2] \cdot \exp(\alpha h)$$
$$+ [-P_2(1-\alpha h) + 4P_3(\alpha h)^2] \cdot \exp(-\alpha h) \quad \text{(6d)}$$

$$A_{SE} = [-P_2(1+\alpha h) + 4P_3(\alpha h)^2] \cdot \exp(\alpha h)$$
$$+ [-P_2(1-3\alpha h) + h^2\theta(Q_2-P_2)/k + 4P_3(\alpha h)^2] \cdot \exp(-\alpha h) \quad \text{(6e)}$$

$$Q_1 = 1/[2\cosh(\alpha h)] \quad \text{(6f)}$$

$$Q_2 = 1/[4(\alpha h) \cdot \cosh(\alpha h) \cdot \coth(\alpha h)] \quad \text{(6g)}$$

$$P_i = \sum_{m=1}^{\infty} \frac{-(-1)^m(\lambda_m h) \cdot \exp(-Z_m k/h^2\theta)}{(Z_m)^i}, \quad i = 2,3 \quad \text{(6h)}$$

$$Z_m = (\alpha h)^2 + (\lambda_m h)^2 \quad \text{(6i)}$$

$$\lambda_m h = (m - \tfrac{1}{2})\,\pi \quad \text{(6j)}$$

The number of terms in the formulation to determine P_i in equation (6h) is dependent on the accuracy desired. Equation (5) can be written for all interior nodal points to form a system of algebraic equations. The system of algebraic equations are then solved to provide the FA numerical solution of the problem.

RESULTS AND DISCUSSION

The exact solution to the one-dimensional transport problem defined by equation (1) with constant concentration boundary condition at the upstream end may be given (Bear, 1979) as

$$\frac{c}{c_o} = \frac{1}{2}\left\{\operatorname{erfc}\left[\frac{x - ut}{(4Dt)^{1/2}}\right] + \exp\left(\frac{ux}{D}\right) \cdot \operatorname{erfc}\left[\frac{x + ut}{(4Dt)^{1/2}}\right]\right\} \quad \text{(7)}$$

where, erfc is the complementary error function; and the initial and boundary conditions are

$c(x,0) = 0, \quad 0 \le x \le \infty$
$c(\infty,t) = 0, \quad t > 0$
$c(0,t) = c_o = \text{constant}, \quad t > 0$

The problem is analyzed for various cases of convective dominant transport with equally spaced grid points and a constant flow velocity equals to 0.5. In order to identify the various cases of solution, the mesh or grid peclet number is defined as $P_e = (u{\cdot}\Delta x)/D$. All the results are expressed in terms of relative concentration ($= c/c_o$).

The performance of the finite analytic method is compared with the exact solution, Crank-Nicholson FD and Galerkin FE solutions. Three cases are given here. The first case is a less convective dominated transport with $P_e = 1$, the second is a moderately convective dominated transport with $P_e = 10$, and the third is a highly convective dominated transport with $P_e = 100$. Numerical results are obtained using $\Delta x = 0.5$ and $\Delta t = 0.4$.

Figures 2, 3 and 4 show profiles of the relative concentration at

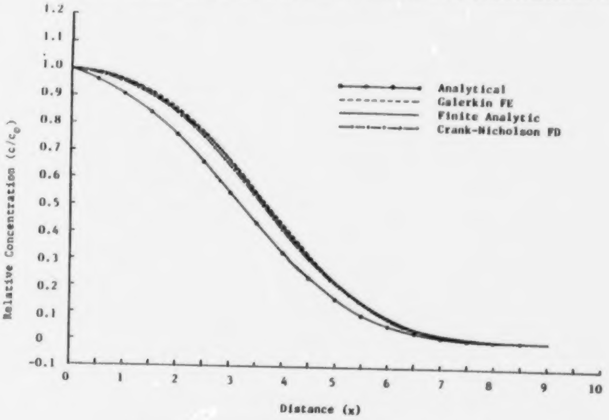

Figure 2. Relative Concentration Profiles at time = 6.4;
$\Delta x = 0.5$, $\Delta t = 0.4$, $u = 0.5$, $D = 0.25$, $P_e = 1$

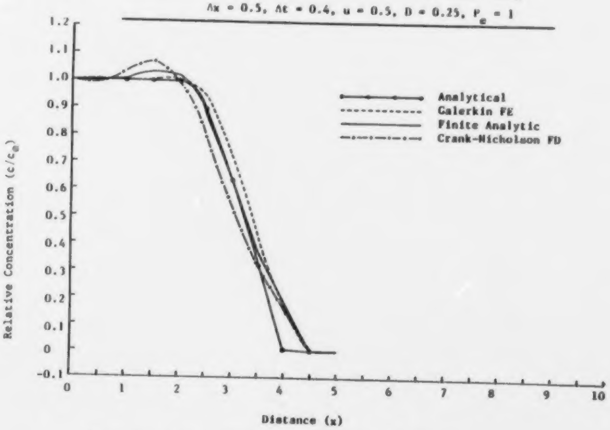

Figure 3. Relative concentration Profiles at time = 6.4;
$\Delta x = 0.5$, $\Delta t = 0.4$, $u = 0.5$, $D = 0.025$, $P_e = 10$

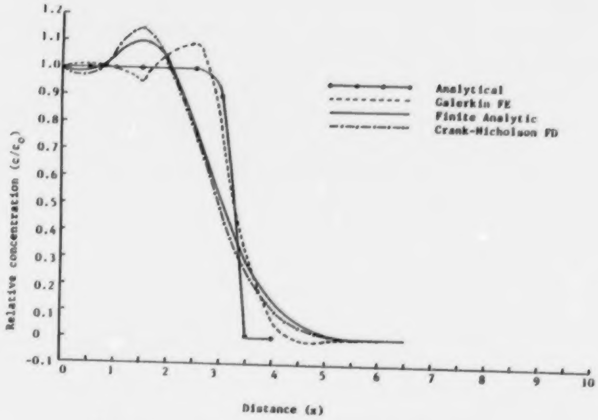

Figure 4. Relative concentration Profiles at time = 6.4; $\Delta x = 0.5$, $\Delta t = 0.4$, $u = 0.5$, $D = 0.025$, $P_e = 100$

$t = 6.4$ for $P_e = 1$ (with $D = 0.25$), $P_e = 10$ (with $D = 0.025$) and $P_e = 100$ (with $D = 0.0025$) respectively. For $P_e = 1$, all three numerical methods are not very much different from each other and the numerical results are fairly alike. Although the results of all the numerical methods for $P_e = 10$ are reasonably close to that of analytical, the gradual development of oscillation is fairly evident. For the highly convective dominated case, $P_e = 100$, the oscillations are observed in all the numerical methods. However, the FA method results are less oscillatory compared to others. Furthermore, the concentration front produced by FD method is considerably more dispersed than that produced by the FA method.

In order to examine the results for temporal oscillations, a spatial location is selected near the upstream end at $x = 0.5$. It may be noted that the relative concentration profile is still away from reaching a steady state condition at this location by the end of time period ($t = 6.4$) considered for this study. Figures 5, 6 and 7 present the profiles of relative concentration for temporal variation at this location for the cases of $P_e = 1$, $P_e = 10$ and $P_e = 100$ respectively. It may be observed in these figures that the solutions resulting from Galerkin FE and Crank-Nicholson FD are more oscillatory in reaching towards the stable condition than the FA method. However, for $P_e = 100$, the FA method produces more dispersed results at the initial time periods compared to the Galerkin FE method.

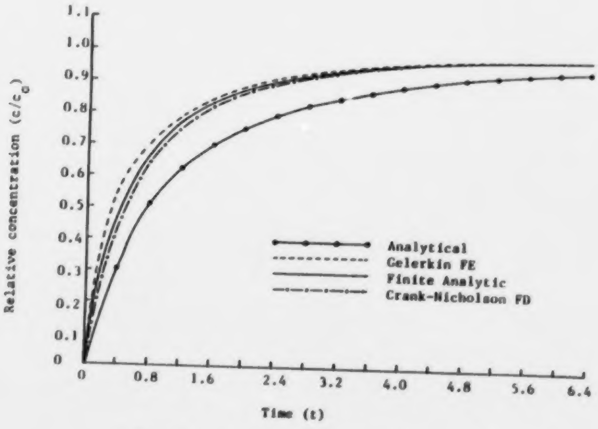

Figure 5. Relative concentration Profiles at $x = 0.5$; $\Delta x = 0.5$, $\Delta t = 0.4$, $u = 0.5$, $D = 0.25$, $P_e = 1$

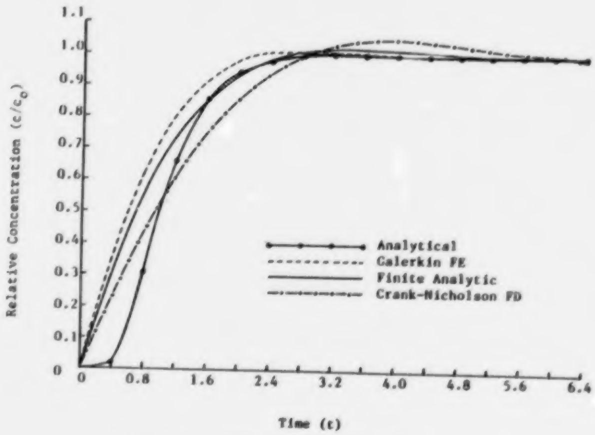

Figure 6. Relative concentration Profiles at $x = 0.5$; $\Delta x = 0.5$, $\Delta t = 0.4$, $u = 0.5$, $D = 0.025$, $P_e = 10$

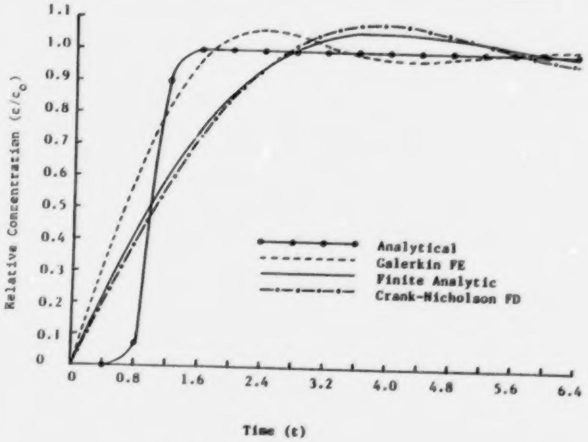

Figure 7. Relative concentration Profiles at $x = 0.5$; $\Delta x = 0.5, \Delta t = 0.4$, $u = 0.5$, $D = 0.0025$, $P_e = 100$.

A comparison of the coefficients of FA method is made with that of the Crank-Nicholson FD scheme. The FA coefficients are estimated from equations (6a) thru (6j), while the equivalent coefficients for the FD method (without upwind scheme) are obtained from expressions given by Forsythe and Wasow (1960). The numerical estimates for the coefficients are presented in Table 1. It is interesting to observe that both the FD and FA coefficients gradually shift upward when the convective transport becomes dominant. However, all FD coefficients on

Table 1 - Coefficients for Various Convective Dominated Solute Transport Problems*

Coefficient Location	Finite Difference Method			Finite Analytic Method		
	$P_e = 1$	$P_e = 10$	$P_e = 100$	$P_e = 1$	$P_e = 10$	$P_e = 100$
WC	0.125	0.0161	0.0017	0.1822	0.0032	0.0995
SW	0.125	0.0161	0.0017	0.2910	0.3147	0.1259
SC	0.25	0.6129	0.6611	0.3540	0.7629	0.9095
EC	0.25	0.1774	0.1678	0.0670	$<10^{-6}$	$<10^{-44}$
SE	0.25	0.1774	0.1678	0.1058	-0.0808	-0.1348

*Above coefficients are estimated for $u = 0.5$; $\Delta x = 0.5$; $\Delta t = 0.4$; $D = 0.25$, 0.025, and 0.0025 (for $P_e = 1$, 10, and 100 respectively).

the west side are the same (i.e., $A_{WC} = A_{SW}$) and so are on the east side (i.e., $A_{EC} = A_{SW}$) too. In addition to this, the coefficients on eastern boundary are greater than the western boundary, indicating a larger role of the step ahead on prediction of the present step. These are physically unrealistic and may be the prime factors responsible for oscillatory and overshoot results. In contrast, the FA coefficients are better distributed with higher weightage to the coefficients on the western boundary of an element than those on the eastern boundary. However, the negative FA coefficients for cases of higher peclet number, although small, are physically unrealistic and may be responsible for overshoot of local numerical results. This may be overcome by changing the boundary approximation to an exponential function instead of second order polynomial function as considered in this study.

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DEVELOPING INFORMATION ON ALDICARB LEVELS IN LONG ISLAND GROUNDWATER

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ABSTRACT

Since the discovery of aldicarb residues in Long Island groundwater in 1979, well over 10,000 soil and water samples on Long Island have been analyzed. Work reported herein couples this extensive data base with further field and laboratory studies to develop a sound scientific assessment of the expected duration and distribution of aldicarb residues in Long Island groundwater.

INTRODUCTION

During the period 1975-1979, TEMIK® aldicarb pesticide was used by potato farmers in Suffolk County, Long Island, for insect and nematode control. Tests conducted in late 1979 and 1980 showed that residues from TEMIK applications did reach potable drinking water supplies.[1] As a result, the use of aldicarb on Long Island was discontinued and studies were begun to assess the extent of aldicarb residues in Long Island groundwater and the length of time these residues would remain.[2,3,4]

Of over 10,000 wells sampled for aldicarb residues in eastern Suffolk County since 1980, about 15% have been found to contain detectable levels of aldicarb residues. The level of residues found in drinking water supplies does not pose a risk to human health.[5] However, the detection of these residues has created public uncertainty and insecurity about their drinking water sources. To alleviate these concerns, the manufacturer has provided carbon filters to remove aldicarb residues from potable water supplies in which concentrations exceed state guidelines. Nevertheless a principal question remains: How long will aldicarb residues persist in groundwater, and at what levels? This paper will report on studies carefully designed to answer this question. Because of space limitation, most data and procedures have been omitted, but are available in an expanded version of the paper, available upon request from the authors.

FIELD PROGRAMS

Three areas of Long Island were selected for detailed study. These three areas (Bayview, Cutchogue, and Wading River) each have different depths to groundwater and, therefore, represent different retention times within the unsaturated zone. In each area, soil cores were taken to determine the amount of residues remaining in the unsaturated zone and about 60 wells were resampled in 1983 and will be sampled again in 1984.

Soil Cores

Two unsaturated zone soil cores were taken from representative fields in each of the three areas during November 1983 or January 1984. At the Cutchogue site, an additional field was sampled at the request of the owner. No aldicarb residues were found at any of the four locations between the surface and 25 feet below the surface. Aldicarb residues were found below 30 feet in one of the cores from the Wading River site and below 60 feet in the other core. The amount of aldicarb residues remaining in the unsaturated zone ranged from 1.2-2.3 lb/acre in the two Wading River cores. This amount, distributed over the lower 70 feet of the unsaturated zone, corresponds to about a third of the amount applied in a single year between 1975 and 1979. Therefore, in areas of Long Island where the water table is deeper than 30 feet from the surface, small amounts of aldicarb residues may be entering the groundwater as a result of applications made prior to 1980.

Well Resampling

In each of the three study areas, about 60 wells which were originally sampled in 1980 were resampled in November 1983. Results from Bayview, the area with the shallowest depth to groundwater, have now been obtained.

Because the distance between the land surface and the water table is shallow (about ten feet) compared to some other parts of Long Island, water containing aldicarb residues would have reached the aquifer sooner in Bayview than elsewhere. Similarly, water recharged to the aquifer after TEMIK was no longer used should have an effect in Bayview sooner than in areas where the depth to water is greater. The aldicarb residue concentration trend in Bayview may serve as an indicator of what will happen in other areas with aldicarb residues.

A total of 43 wells in the Bayview area were sampled in both 1980 and 1983. Of these, 27 contained detectable concentrations of aldicarb residues in one or both years. Table I summarizes some statistics about the concentration of aldicarb residues in those 27 wells. The average concentration of aldicarb residues in these 27 wells dropped from 47 ppb to 27 ppb. The number of wells containing detectable residues dropped from 27 to 24, but the number of wells with aldicarb residue concentrations greater than 7 ppb rose from 15 to 19. Thus, although the aldicarb residue concentration dropped dramatically in some of the wells with the highest concentrations in 1980, the concentration in other wells rose. The drop in the average concentration is a positive sign that is probably caused by three major factors: reduction of the amount of aldicarb residues entering from the unsaturated zone, degradation of aldicarb residues, and the movement of some of the aldicarb residues into the bay.

TABLE I

ALDICARB CONCENTRATION STATISTICS FOR BAYVIEW
FOR 1980 AND 1983

	1980	1983
Average aldicarb concentration in wells containing residues in either sampling	47 ppb	27 ppb
Total number of wells with aldicarb residues	27	24
Number of wells with aldicarb concentrations exceeding 7 ppb	15	19
Of the 27 wells with residues, number of wells in the range of:		
150-200 ppb:	3	0
100-150 ppb:	3	1
50-100 ppb:	3	1
7- 50 ppb:	6	17
1- 7 ppb:	12	5
Less than 1 ppb:	0	3

The movement of the aldicarb residue plume is demonstrated by the statistics in Table II which show that levels of aldicarb residues dropped in some wells within 400 feet of a potato field, but rose in some wells further away than 400 feet. However, for the wells tested in the Bayview area, wells containing residues in 1983 also contained residues in 1980.

TABLE II

ALDICARB CONCENTRATION TRENDS

Well Category	Number of Wells Where the Aldicarb Concentration: Went up More than 10 ppb	Went down More than 10 ppb	Was Stable Within 10 ppb
Less than 400 feet from potato field	0	9	3
More than 400 feet from potato field	3	0	12
TOTAL	3	9	15

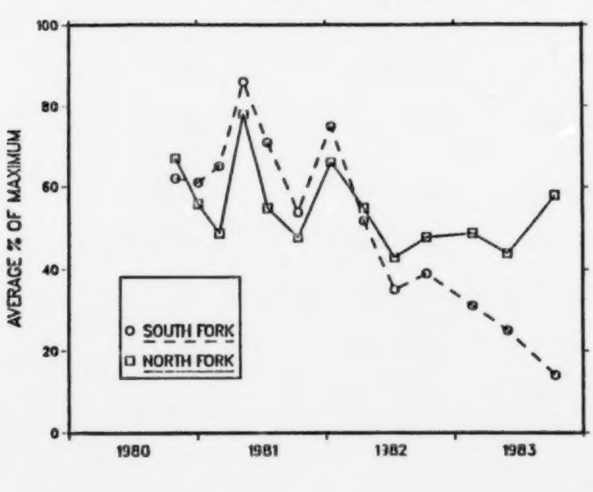
The analysis of results from the other two areas have not yet been completed. However, the average level of residues actually increased from 1980 to 1983 in the Wading River area, aldicarb residues from 1975 and 1976 applications were just entering groundwater in 1980. As demonstrated by the soil cores taken in this area, small amounts of aldicarb residues are still entering the aquifer. The resampling of wells to take place in 1984 will help define the current concentration trend in the Cutchogue and Wading River areas.

Well Monitoring Data

Selected private potable water wells have been monitored regularly since November 1980, as part of a program by the Suffolk County Health Department and Union Carbide to provide information on carbon filter performance and on aldicarb residues in groundwater. Although the wells were not selected to provide an indication of average aldicarb residues concentrations on Long Island, they do provide information about possible trends in residue levels. The aldicarb residue levels in these wells vary widely making data interpretation more difficult. To account for these variations in concentration, data from each well was normalized by dividing by the maximum concentration detected in that well and then averaging the normalized data for each sampling interval.

The results presented in Figure 1 show that concentration of residues in the monitoring wells are declining. On the South Fork residue levels are about 14% of the maximum readings, whereas residue levels on the North Fork have declined to levels about half of the maximum readings. Since the hydrologeology of the two areas is similar, one explanation for the difference between the North and South Fork decline rates is the heavier use of TEMIK on North Fork potato farms, especially during 1975 through 1977.

Figure 1 Data from Frequently Sampled Long Island Wells



LABORATORY RESEARCH

Accurate determination of the degradation rate of pesticide residues in groundwater by experiments in the field is difficult, because the residues are subject to movement, dilution and recharge in addition to degradation. Therefore, pesticide degradation rates can best be determined from controlled laboratory experiments. Two types of experiments are usually performed. One is to conduct laboratory degradation experiments using soil and water from specific sites of interest. The second is to measure degradation rates in distilled water solutions. The distilled water experiments are easier to perform but the results are not as meaningful as soil and water experiments because microbiological and soil catalytic effects are ignored.

Soil and Water Degradation Study

Estimated rate constants and corresponding half-lives from degradation studies using actual Long Island samples are presented in Table III. Because the study has been underway for only 17 months and the half-life of aldicarb residues in Long Island groundwater is expected to be at least two to three years based on distilled water studies, results from the study (expected to last six years) are only preliminary. The rate values for which there are significant correlation coefficients are the autoclaved samples at 5 and 25°C and the non-autoclaved samples at 25°C. Thus far, no statistical difference exists between the sterile and non-sterile samples at temperatures of 5 and 13°C. Therefore, biological degradation does not appear to be an important degradation mechanism in Long Island groundwater (temperature of about 10°C). The data also show a decline in degradation rate with decreasing temperature. Although the results from this study are only preliminary and the confidence interval is quite wide, the half-life corresponding to the center point in the confidence interval appears to be in agreement with earlier projections of 2-3 years.[6].

TABLE III
PRELIMINARY ESTIMATED RATE CONSTANTS AND HALF-LIVES
FROM LONG ISLAND SOIL AND WATER DEGRADATION STUDY

	Rate Constant (days^{-1}) Estimate	Standard Deviation	Half-life (days) Estimate	95% Confidence Int.
Autoclaved (Sterile)				
5°C	0.000710	0.000166	976	(627, 2190)
13°C	0.000845	0.000216	820	(510, 2090)
25°C	0.00324	0.000431	214	(162, 313)
Non-Autoclaved				
5°C	0.000224	0.000282	3022	(771, ---)
13°C	0.000757	0.000513	916	(351, ---)
25°C	0.00858	0.00196	81	(52, 177)

Distilled Water Hydrolysis Studies

Because of the ease by which these studies can be performed compared to soil and water studies, hydrolysis studies by several different researchers have been performed.[6,7,8,9] In general, these studies show that the hydrolysis of aldicarb is much slower than aldicarb sulfoxide or aldicarb sulfone and that the rate of hydrolysis generally increases with increasing temperature and pH.

The current study was designed to be a comprehensive study which builds upon the information gained from previous studies. Data will be collected for aldicarb sulfoxide and aldicarb sulfone over a six year period at six pHs (4, 5, 6, 7, 8, and 9) and four temperatures (15, 25, 35, and 45°C). The time-intervals at which individual samples are analyzed are not the same for all combinations, but instead the times between analyses are adjusted based on interim results to generate data which will span at least four half-lives. Preliminary half-life estimates (calculated from first-order reaction rate constants) from the hydrolysis study are presented in Figures 2 and 3. Due to the slower hydrolysis rate at lower temperatures and pH, enough time has not elapsed from the start of the experiment to allow preliminary estimates to be made at these conditions. The available results indicate that the hydrolysis rate is faster than predicted by Hansen and Spiegel[5] at high pH but slower at pH values below 7.

The data show that above pH 5 the logarithm of hydrolysis rate of either aldicarb sulfoxide or aldicarb sulfone is a linear function of pH. Hydrolysis studies[7] of aldicarb sulfoxide and aldicarb sulfone at pH values greater than 11 and at 15 and 25°C show a linear relation between hydrolysis rate and hydroxide ion concentration which can be extrapolated at lower pH values. Half-life values calculated from these extrapolations correlate well with those obtained so far in this study at pH values between 5 and 9. Around a pH of 5, the hydrolysis rate for aldicarb sulfoxide decreases with increasing or decreasing pH so the minimum hydrolysis rate at a given temperature occurs at pH 5. For aldicarb sulfone, the pH appears to have little effect below pH 5. The hydrolysis rate around pH 5 will be better defined later in the study when more data in this region become available.

Discussion of Laboratory Degradation Data

The half-life values obtained from the soil and water degradation studies were compared to distilled water hydrolysis half-lives. Degradation rates at these locations were measured using a procedure similar to that described for the Long Island samples. These degradation rates are similar to those reported by Smelt et al[10] for anaerobic subsoils.

For the locations listed in Table IV, the half-lives measured in the soil and water degradation experiments are a factor of 3 to 80 shorter than half-life estimates based on distilled water hydrolysis. Part of the increased degradation rate in the soil and water samples is due to microbial degradation processes, especially for the Florida locations. However, the studies conducted with Long Island samples at 5 and 13°C showed no significant difference in degradation rates between sterile and non-sterile samples. Therefore, at least part of the increase in degradation rates is due to non-biological effects.

Figure 2

Effect of Temperature and pH on Chemical Hydrolysis of Aldicarb Sulfoxide

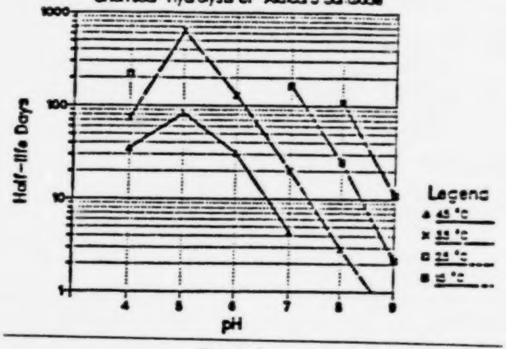


Figure 3

Effect of Temperature and pH on Chemical Hydrolysis of Aldicarb Sulfone

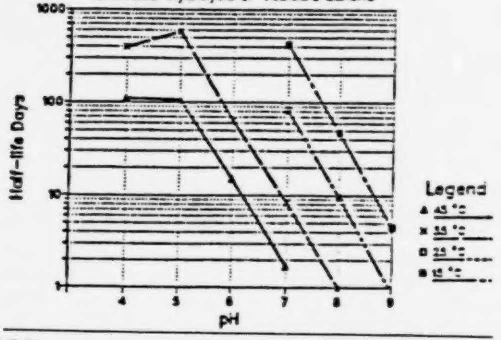


TABLE IV

COMPARISON OF DEGRADATION RATES OF ALDICARB RESIDUES ESTIMATED BY HYDROLYSIS WITH DEGRADATION RATES MEASURED IN SOIL AND WATER DEGRADATION STUDIES

Sample Location	Residues Present	Sample pH	Study Temp. (°C)	Measured Half-Life (days)[1]	Est. Half-Life Based on Distilled Water Hydrolysis (days)	Estimated/ Measured
Long Island[2]	Sulfoxide and Sulfone	6	13	916 (351, —)*	3000 - 5000	4
			25	81 (52, 177)*	600 - 1000	10
Wisconsin Central Sands	Sulfoxide and Sulfone	7	25	14 (12, 16)	80 - 160	9
	Sulfone Only	7	25	13 (10, 16)	80	6
North Carolina Coastal Plain	Sulfoxide and Sulfone	5	25	67 (62, 74)*	5000 - 6000	80
	Sulfone Only	5	25	149 (83, 655)*	6000	40
Florida Locations						
Lutz	Sulfoxide and Sulfone	6	25	49 (41, 61)	600 - 1000	16
Lake Hamilton	Sulfoxide and Sulfone	6	25	47 (40, 55)	600 - 1000	17
Alcoma	Sulfoxide and Sulfone	6	25	49 (38, 63)	600 - 1000	16
Oviedo	Sulfoxide and Sulfone	7	25	3 (1, 5)	80 - 160	40
Fort Pierce	Sulfone only	7	25	29 (21, 47)*	80	3

1. Numbers in parenthesis are the 95% confidence limits.
2. Non-autoclaved samples.

*Preliminary estimate which will be refined as more data becomes available.

CONCLUSIONS

Preliminary results from the shallow groundwater field site and monitoring wells indicate that the average concentration of aldicarb residues on Long Island is dropping. The decline of residues in areas where relatively deep groundwater is present is less apparent due to the continuing recharge of residues into groundwater from the unsaturated zone.

Preliminary results from laboratory studies indicate that the half-life of aldicarb residues is approximately 2-3 years in Long Island groundwater. Laboratory studies show that estimates of half-lives obtained from distilled water hydrolysis studies are longer by a factor of 3-80 when compared with studies using actual soil and water samples from the specific locations.

The results from the field and laboratory studies being conducted will be incorporated into calculations describing degradation and movement of aldicarb residues in the three selected field areas on Long Island. When completed, this assessment will provide a more secure basis for predicting the future impact of aldicarb residues on Long Island drinking water wells.

ACKNOWLEDGMENTS

The participation of the Suffolk County Department of Health Services in the field work, including the collection of water samples, is acknowledged. Unsaturated zone soil cores were obtained with the assistance of James Pike, T.E. Marquardt, and J.P. Cartier. Beth Snowden and J.L. Hansen assisted in data analysis. Laboratory studies were performed by Linda Wagenet and R.R. Romine.

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SPRINGS ARE MORE EFFICIENT AND RELIABLE THAN WELLS FOR MONITORING GROUND WATER QUALITY IN MOST LIMESTONE TERRAINS - A CONSEQUENCE OF TRANSPORT PROCESSES OCCURRING IN CONDUITS

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ABSTRACT

In maturely karsted areas, where carbonate bedrock is above the water table, infiltration water percolates vertically until it intercepts a cave system in which most flow is: 1) nearly horizontal, 2) in conduits, 3) convergent, generally dendritic or trellised, 4) generally in the uppermost fringe of the phreatic zone, and 5) to a spring (or group of springs) that drains an entire groundwater basin. The flow in a large conduit is in many ways analagous to flow in a surface river. The trunk flow of both is fed by tributaries and by diffuse flow through the surrounding rock or sediment; but most of the flow to a conduit is at a higher velocity than it is to a surface river, and it is through vertical joints and bedding planes rather than pores.

The only sure way to sense the active flow from a site to be monitored is to intercept the conduit system that drains it. And unless one can prove (generally by dye-tracing) that a particular cave stream drains all of the site, springs -- rather than observation wells -- are the most efficient, reliable, and economical places to monitor for pollutants in most limestone terrains where carbonate rock is in the vadose zone! This is because the probability of a randomly located drill hole intersecting such a conduit is almost nil. A plan to guarantee sensing of the conduit system should include: 1) location of springs along streams and in sinkhole bottoms, 2) dye-tracing to show the presence or absence of flow routes, and 3) judicious selection of springs as leachate-monitoring and background-monitoring sites, as discussed in the text. The plan may include monitoring of cave streams and mapping of the potentiometric surface and of groundwater basin boundaries.

PROLOGUE

The conclusion stated by the title of this paper may seem a bit peculiar to some readers. But let us remind them that it is not the result of an afternoon spent tinkering with groundwater models at a computer console. Rather, it is based on a summary of 50 years of research and consulting experience in 20 states and 20 countries. It is also based on an analysis of the theoretical geochemistry and hydrology, model studies (Ewers, 1982; Ewers and Quinlan, 1981), observations made in the field and underground, monitoring wells drilled to intercept cave streams, mapping of the potentiometric surface in 40 groundwater basins, more than 500 dye-tests, and a review of the world karst literature. The conclusion is original and not known to be in any published report or paper.

INTRODUCTION

When an observation well is drilled for monitoring the quality of groundwater that drains from a surface site, it is assumed that flow is: 1) through a granular or fractured medium, 2) dispersive as a result of advection, hydrodynamic dispersion, and molecular diffusion, and 3) in a plume to be intercepted by the well. If the site overlies maturely karsted limestone or dolomite, an alternative assumption might be made; 4) that the flow will be to a cave stream that: a) drains the site to be monitored and b) is intercepted by the well. In most karst terrains, however, these four assumptions are invalid.

GROUNDWATER FLOW IN KARST

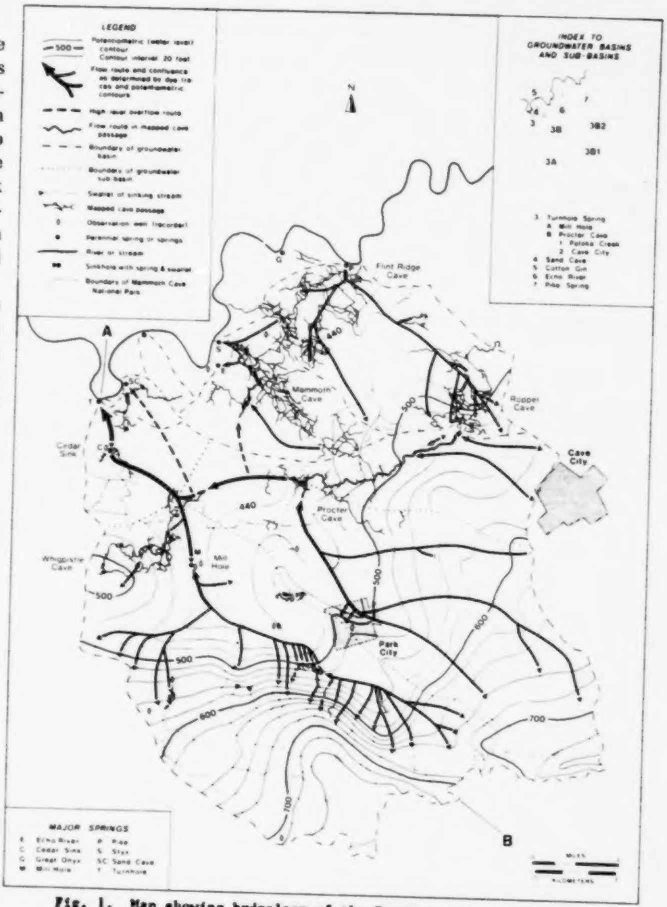

Fig. 1. Map showing hydrology of the Turnhole Spring groundwater basin (near Mammoth Cave, Ky.), sub-basin boundaries, potentiometric surface, flow routes, springs, caves, and observation wells. A northwest-southeast cross section of this map area is shown in figure 2. Note that there is a correlation between troughs on the potentiometric surface and the axes of major drainage through caves, and also that there is both a dendritic and locally trellised drainage pattern of groundwater flow. Of special importance are three highlevel overflow routes that convey groundwater, sometimes sewage-laden, out of the Turnhole Spring basin to three different basins to the north. The eastern-most of these overflow routes is in Roppel Cave, and is not shown by a dashed line. This map, modified after Quinlan and Ray (1981), is based on more than 60 dye-traces, more than 150 water level measurements, and mapping of more than 350 miles of cave passage; this map is more detailed than would be necessary for the evaluation of a particular waste disposal site. The hydrology of this area has been summarized by Quinlan et al. (1983), Quinlan and Ewers (1981), and Quinlan and Ray (1981).

In maturely karsted areas in which carbonate rock is above the water table, infiltration water percolates vertically until it intercepts a cave stream in which most flow is: 1) nearly horizontal, 2) in conduits, 3) convergent, generally dendritic or trellised, as shown in Figure 1, 4) generally in the uppermost fringe of the phreatic zone, and 5) to a spring (or group of springs) that drains an entire groundwater basin, as shown in Figures 1 and 2. The flow in a large conduit is, in many ways, analagous to flow in a surface river. For example, the trunk flow

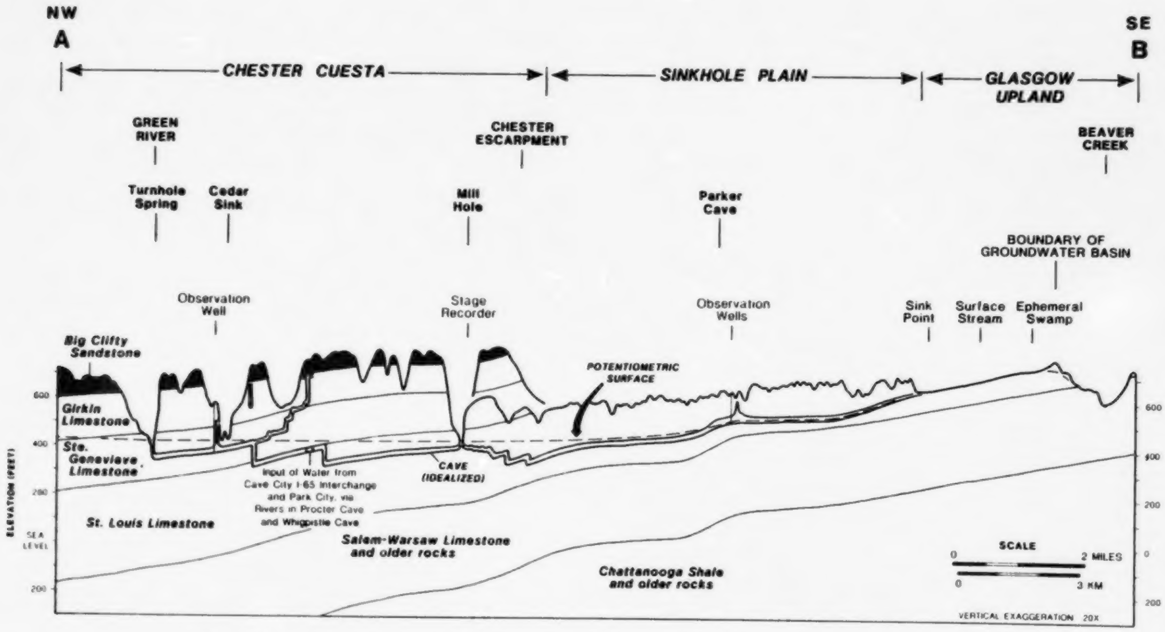

Fig 2. Cross section along the axis of major drainage in the Turnhole Spring groundwater basin, depicting flow of water to the northwest, as shown in figure 1. The line of the section is oblique to the east-west strike of the beds. Also shown are stratigraphy, stucture, caves, potentiometric surface, observation wells, and physiography.

of both is convergent and fed by tributaries and by diffuse flow through the subjacent (or surrounding) bedrock or sediment. But most of the flow to a conduit is at a higher velocity and through vertical joints and bedding planes rather than pores.

In the lower reaches of a karst groundwater basin, however, the flow may be divergent rather than convergent, although most flow is still confined to conduits. The conduit pattern there may be distributary, in the form of a vertible "underground delta" that may be up to several miles wide (Ewers, 1982, Quinlan, et al., 1978; and Ewers, et al., 1978). But no matter whether the flow is convergent or divergent, springs—rather than wells—are the most efficient, reliable, and economical places to monitor for pollutants in most limestone terrains. This is because the probability of randomly-located drill holes intersecting an active conduit system is almost nil. A well drilled into a fracture-trace lineament, if present, may miss the trunk conduit that might also be present. In our experience, few trunk conduits are directly beneath a lineament.

DESIGN OF GROUNDWATER MONITORING NETWORKS

The design of a groundwater monitoring network in a maturely karsted area should include the following in order to guarantee sensing of the conduit system that drains a particular surface site: 1) location of major springs along river banks and of stream resurgences at the bottom of sinkholes, 2) dye-tracing to establish the relation between the site to be monitored and the springs and other resurgences that do and do not drain the site (dye-tracing should, if possible, be made during both low-flow and high-flow conditions because flow routes that function only during moderate- to high-flow conditions may divert some of the water in a groundwater basin to springs in one or more adjacent basins), 3) monitoring of the place (or places) shown by dye-tracing to drain the surface site and, 4) monitoring of at least one hydrogeologically similar spring that doesn't drain the surface site, as a valid control on background levels of contaminants.

It may also be expedient to: 1) Use dye-tracing to delineate groundwater boundaries (Quinlan and Ray, 1983), 2) map the large streams of major caves, if the latter can be found, 3) use dye-tracing to show the relationship of these cave streams to the site to be monitored, 4) drill wells to intercept and monitor such cave streams (The surface location of a drill hole to intercept a known cave stream can be determined by conventional surveying techniques or by using magnetic induction equipment, as discussed by Reid, 1984.), and 5) where possible, map the potentiometric surface.

The most practical dyes to use for dye-tracing are: fluorescein, optical brightener, Direct Yellow No. 96, and, to a lesser extent, Rhodamine WT. The techniques for using them are summarized by Quinlan and Ewers (1981, p. 502-504). In general, radioactive tracers should be avoided—for numerous reasons.

The oral presentation of this paper included discussion of additional examples of well-delineated flow systems and a leachate monitoring network.

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EFFECT OF STOCHASTIC INPUTS AND PARAMETERS IN SOLUTE-TRANSPORT MODELING

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ABSTRACT

Successful planning, design and regulatory evaluations should be based on both deterministic and stochastic techniques, but most scientists and engineers, even while employing very sophisticated mathematical tools, treat solute-transport calculating as if they were only deterministic. In conventional solute-transport predictions, random variables and uncertain model parameters are replaced by their expected values and the resulting deterministic model is solved.

An approach of this type can be misleading and results in the use of an arbitrary softy or overdesign factors to accommodate the reality of uncertainty. While the introduction of stochastic methods into solute-transport modeling activities cannot reduce the uncertainty, the practice can lead to more precise statements about the uncertainty, and, therefore, to better decision making. With stochastic analysis, it becomes possible to make statements such as: At the point of interest, the concentration interval of 5.0 to 10.0 mg/l includes the expected value with a probability of 0.95.

The use of Monte-Carlo methods to introduce stochastic variables into a deterministic analytical solute-transport model is demonstrated. This approach can account for uncertainties in boundary conditions, such as input flow rates and concentrations, as well as uncertainties in model transport coefficients, such as hydraulic conductivity and hydrodynamic dispersion coefficients. The model inputs are characterized in terms of their statistical properties, i.e., mean and variance.

The results of this stochastic modeling approach include not only the expected value of concentration at a point of interest, but also the frequency distribution for the concentration based on uncertainties in the model input and transport parameters. The frequency distribution can be used to assess the risk posed by the release a chemical substance into the subsurface environment.

Information gained by a stochastic analysis can also be used to decide whether parameters on a deterministic model have been evaluated with sufficient precision for use in a simulation. This "sensitivity" analysis can provide information which is useful in planning field activities and/or additional modeling efforts.

Finally, the introduction of randomness or uncertainty into a model must reflect what is physically happening in the process to the extent possible. Caution must be exercised to assure that randomness in correlated parameters, such as interstitial velocity and porosity, are introduced in a manner such that the model response approximates the response of the physical system. Autocorrelation methods can be used to accomodate correlated model parameters.

INTRODUCTION

Flow through aquifers and the transport of dissolved contaminants traditionally are modeled by deterministic partial differential equations. This approach is based on the sound principal of conservation of mass and the dynamics of flow are represented by Darcy's law. However, there is always some uncertainty as to the proper choice of the flow and solute-transport equations. This model uncertainty arises from the many assumptions that must be made to keep the analysis tractable. Each assumption affects the results of the model to an undetermined, but hopefully, small extent. Examples of model uncertainty include the use of Darcy's law, even when it is only marginally applicable; the use of linear partial differential equations, even when the actual behavior is nonlinear; and the use of a potential flow model for hydrodynamic dispersion phenomena, which may be attributed to several physical processes occuring simultaneously. Model uncertainties are very important, but will not be considered in this paper. Instead, an appropriate mathematical model is assumed to be available that adequately describes the solute transport process. With this assumption, the future concentration distributions are determinant and predictable provided the initial and boundary conditions, the model parameters, and the forcing functions can be specified exactly.

Model input parameters are estimated from a few discrete observations and assumptions and are seldom completely determined. Even if the assumption is made that the data contain no measurement or analytical errors, the estimates of system variables would still be certain to some extent. A more logical approach would be to define an ensemble of possible values, each having a certain probability of realization. In other words, each variable in the deterministic model is represented by a probability density function rather than a single estimated value. The deterministic model is equally applicable to any point in this ensemble and, therefore, will define a corresponding ensemble with corresponding probabilities in the model solution space. The equations describing the behavior of the system become equations for random functions or stochastic differential equations. In addition to following the physical laws of conservation of mass, Darcy's law, and physical/chemical reactions, the stochastic differential equations for flow and/or solute transport take into account the stochastic nature of the system. Since system randomness can be taken into consideration explicitly in such models, these models, sufficiently developed, may led to more realistic decision making.

Stochastic models can evolve through two main approaches. One approach that has been used to describe flow and dispersion processes in porous media is to directly employ probabilistic concepts to small subdivisions of the system (Bakr, et al., 1978; Chirlin and Dagan, 1980; Dagan, 1979, 1981, 1982a, 1982b; Delhomme, 1979; Dettinger and Wilson, 1981; Gelhar, et al., 1979; Gutjahr, et al., 1978; Neuman and Yakowitz, 1979; Neuman, et al., 1980; Neuman, 1980; Prickett, et al., 1981; Sager, 1978, 1979; Scheidegger, 1954; Simmons, 1982; Smith and Schwartz, 1980, 1981; Tang and Pinder, 1979). This approach is very attractive since the solution of the resulting stochastic partial differential equations directly yields the parameters of the probability density functions describing the solution space. These models are comparatively easy to formulate, but their solution entails currently unsolved mathematical problems (Sager, 1978). The theory of linear partial differential equations and nonconstant coefficients is far from complete, and for random coefficients the situation is even worse (Frisch, 1968). The principal difficulty arises from the fact first observed by Kraichman (1962) that in spite of its apparent linearity, the equation is nonlinear in stochastic quantities. Since the solution of a linear equation depends nonlinarly upon the coefficients, even the lowest order moments of the solution depend on the complete set of all of the moments of the coefficients. Thus only relatively simple problems are solvable.

Another approach to the development of a stochastic model for fluid flow and/or solute transport in aquifers is the application of a Monte Carlo simulation of the process defined by the deterministic model. This approach has been used in the design and optimization of chemical processes (Al-Zakri and Bell, 1981; Berryman and Himmelblau, 1971, 1973; Buckley, 1950; Dittmar and Hartmann, 1976; Grossman and Sargent, 1978; Lashmet and Szczepanski, 1974; Lin and Slattery, 1982; Takeichiro, et al., 1970; Weisman and Holzman, 1972; Wen and Chang, 1968) and to a lesser extent in ground-water flow (Cooley, 1977, 1979; Rao, et al., 1981; Smith and Freeze, 1979a, 1979b; Tang and Pinder, 1979). Knowing the probability density function for each variable in the deterministic model, random numbers generated from a distribution having the same moments are substituted for the variables in the deterministic model. By repeatedly sampling the input parameter distributions and solving the deterministic model, the probability density function of the model response can be generated.

Monte Carlo simulations represent a "brute force" approach compared to the direct solution of a stochastic partial differential equation. Monte Carlo methods avoid the mathematical problems associated with nonconstant coefficients and can be applied to nonlinear systems as well as linear systems. The main disadvantage is that large sample sizes may be required to adequately define the probability density functions in the model solution space. Each sample requires the solution of the deterministic model. Neither approach is more "correct" than the other, since the models are only approximations in any case. However, in both approaches the introduction of randomness into the model should reflect what is happening physically in the process to the extent possible.

The application of a Monte Carlo simulation to a two-dimensional solute transport model is presented in this paper. The intent is to demonstrate one approach to introducing parameter uncertainty into deterministic solute transport models and the effect of this one type of uncertainty on model results. This example is somewhat oversimplified in that autocorrelation between aquifer parameters, such as porosity and permeability, and correlation of forcing functions with time have been neglected. However, correlation of input parameters may be very important in the correct interpretation of many stochastic models.

EXAMPLE OF MONTE CARLO SIMULATION

The example problem is based on the dispersal of chromium discharged to the ground water is southeastern Nassau County, New York. The hydrogeology and history of contamination have been documented by Perlmutter and Lieber (1970) and will be briefly summarized in the following paragraphs.

Site Location

The general area of the documented case history of the concentrations of contaminants in ground water is in southeastern Nassau County, Long Island, New York. The detailed study area included an industrial park at South Farmingdale. During World War II, the industrial park was occupied by an aircraft company whose cadmium and chromium enriched metal plating waste was the source of much of the heavy-metal contamination in a shallow glacial aquifer.

Hydrogeology

The upper glacial aquifer, which is addressed in this document, extends from the water table, at depths ranging from 0 to 15 feet below the ground surface, to the top of the deeper Magothy aquifer, at depths of 80 to 140 feet below the ground surface. The upper unit consists of beds and lenses of fine to coarse sand and gravel. In some parts of the aquifer, thin lenses of fine to medium sand, as well as some silt, are interbedded with the course material. Data from scattered well borings indicates that the lower 8 to 10 feet of the upper unit may consist of silty and sandy clays.

The principal direction of ground-water flow in the upper glacial unit is from north to south. The regional hydraulic gradient is approximately 0.0025 ft/ft and the average coefficient of permeability is assumed to be 1,600 gal/day/ft^2 with an average porosity of 0.35 (Perlmutter and Lieber, 1970). The ground-water movement is horizontal throughout the area of interest, with the exception of local recharge and discharge areas where vertical or oblique flow may be predominant.

Plating-Waste Contamination

The chromium contamination in the upper glacial unit was derived principally from the disposal of metal-plating and anodizing waste water to unlined basins. During World War II, and for several years thereafter, essentially untreated plating-water effluent was recharged to the aquifer through these disposal basins. Perlmutter and Lieber (1970) estimated that during the early 1940's as much as 200,000 to 300,000 gallons of effluent containing approximately 52 pounds of chromium was discharged daily into the upper glacial unit. At the end of World War II, the amount of plating-waste effluent was decreased substantially and a chromium removal unit was installed in 1949.

By 1949, or approximately 9 years after the start of plating-waste disposal, a plume of contaminated water had migrated southward approximately 3,900 feet with a maximum width of about 850 feet. Maximum observed chromium concentration was approximately 40 mg/l.

Since 1949 the chromium concentrations decreased substantially in nearly all sections of the plume. The maximum observed chromium concentration was about 10 mg/l in 1962. However, the plume of contaminated water had migrated farther southward beyond Massapequa Creek, a small stream which serves as a natural drain for part of the contaminated ground water. The plume was approximately 4,300 feet long with a maximum width of almost 1000 feet in 1962.

Analytical Model

The governing differential equation, which is assumed to describe the conservation of mass in this situation, can be written as

$$R_d \frac{\partial C}{\partial t} + V^* \frac{\partial C}{\partial x} = (\alpha_x\ V^*) \frac{\partial^2 C}{\partial_x^{\ 2}} + (\alpha_y\ V^*) \frac{\partial^2 C}{\partial_y^{\ 2}} - R_d\ \lambda C \qquad (1)$$

where

C = concentration of tracer in solution,
R_d = retardation coefficient,
t = time,
V^* = average intersititial velocity,
x = distance in the direction of ground-water flow,
y = horizontal distance normal to the direction of ground-water flow,
α_x = longitudinal dispersivity,
α_y = transverse dispersivity,
λ = first-order decay constant.

A solution to Equation 1 is (Hunt, 1978; Wilson and Miller, 1978):

$$C = \frac{C_o\ Q'}{4\pi\theta\ (D_x^*\ D_y^*)^{0.5}}\ \mathrm{EXP}\ \left(\frac{V_x^*}{2D_x^*}\right)\ W(U,B) \qquad (2)$$

where θ is the effective porosity of the aquifer, Q' is the volumetric source rate per unit depth of aquifer with a tracer concentration of C_o, and $D^* = \alpha V^*$ is a dispersion coefficient. The term W(U,B) is commonly referred to as the "well function for leaky artesian aquifers" (Hantush, 1956) with

$$U = \frac{\left(\frac{V_x^*}{D_x^*}\right)^2 + \frac{D_x^*}{D_z^*}\left(\frac{V_y^*}{D_x^*}\right)^2}{\frac{4V^2 t}{R_d\ D_x^*}} \qquad (3)$$

and

$$B = \frac{1}{2}\left[\left(\frac{V_x^*}{D_x}\right)^2 + \frac{D_x^*}{D_y^*}\left(\frac{V_y^*}{D_x^*}\right)^2\right]^{1/2} \left[1 + \frac{4D_x^*\ R_d\ \lambda}{V^{*2}}\right]^{1/2} \qquad (4)$$

The data required for this deterministic model are summarized in Table 1. The following paragraphs will discuss the estimation of these model parameters based on the limited field data, judgement, and experience.

Table 1

Input Data for Analytical Solute-Transport Model

Variable	Minimum	Average	Maximum
Saturated Thickness, ft	105	110	115
Effective Porosity	.34	0.35	.36
Interstitial Velocity, ft/dy	1.45	1.50	1.55
Longitudinal Dispersivity, ft	69	70	71
Transverse Dispersivity, ft	13	14	15
Retardation Coefficient	1.0	1.0	1.0
First-order Decay Constant, dy^{-1}	0.0	0.0	0.0
Source Loading, lb/dy	51	52	53

Assuming that the water table is located approximately at the ground surface, the average saturated thickness of the upper glacial unit can be estimated from the depth to the top of the deeper Magothy aquifer. Thus, the average saturated thickness, S_t, will be taken as:

$$S_t = \frac{80 + 140}{2} = 110 \text{ ft}$$

The superficial, or Darcy, velocity can be estimated from the average coefficient of permeability, K, and the regional hydraulic gradient, dh/dx. From Darcy's law

$$V = - K \frac{dh}{dx}$$

where the minus sign indicates that the flow is in the direction of decreasing hydraulic head. Thus

$$V = \frac{1600 \text{ gal}}{\text{day ft}^2} \; \frac{\text{ft}^3}{7.48 \text{ gal}} \; \frac{0.0025 \text{ ft}}{\text{ft}}$$

and

$$V = 0.52 \text{ ft/day}$$

The average interstitial, or pore, velocity, V*, can be estimated by assuming that the areal porosity is equal to the volume porosity, θ, and

$$V^* = \frac{V}{\theta}$$

Using the estimated value of total porosity

$$V^* = \frac{0.52 \text{ ft/day}}{0.35}$$

or

$$V^* = 1.5 \text{ ft/day}$$

The longitudinal and transverse disperison coefficients are the most difficult parameters to estimate. Based on the results of a numerical model for the same site, Pinder (1973) estimated longitudinal and transverse dispersivities, of 69.9 and 14.0 feet, respectively.

Chromium is believed to be a conservative material in this system (Perlmutter and Lieber, 1970), and both adsorption and chemical/biological decay can be neglected. Therefore, $K_d = 0$ (or $R_d = 1$) and $\lambda = 0$.

The last set of model input data to be specified is the source mass/rate schedule. A steady mass rate of 52 lb/day of chromium will be assumed from the time of initial injection to mid-1949, or approximately 2800/days. At this time, the actual extent of the contamination was estimated; and the chromium removal unit was installed. The actual volumetric rate and concentration of the source of chromium contamination are not required. However, the units of the source term must be consistent with other parameters in the model. The mass rate of chromium can be converted to units of concentration times volume rate per unit depth of aquifer as follows:

$$\frac{C_o \text{ lb}}{\text{day}} \; \frac{454 \times 10^3 \text{ mg}}{\text{lb}} \; \frac{\text{ft}^3}{28.321 \text{ liter}} \; \frac{1}{m \text{ ft}}$$

$$= 16{,}030 \text{ (mg/liter)(ft}^3\text{/day)/ft}$$

for 2800 days.

The model input data for this example problem are summarized in Table 1. Triangular probability density functions were chosen for ease of visualization in this example, with upper and lower limits being selected more or less arbitrarily.

The average values of the model parameters were used in the deterministic model to calculate the concentration at Massapequa Creek (x = 4200 ft, y = 0 ft) after 2800 days of plating-water recharge to the aquifer from the disposal basins. The calculated concentration is 8.38 mg/l at this time and distance from the source. This single value represents the results of a deterministic modeling approach.

A Monte Carlo simulation was then carried out using the same data. The frequency distributions of the calculated concentration with a sample size of 128 is presented in Figures 1 and 2. The relative fre-

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                    UNCERTAINTY MODEL                                OUTPUT PAGE
       --POLLUTANT CONCENTRATION  FOR A LEACHATE PLUME                  1        --



SAMPLE SIZE FOR CONCENCENTRATION (MG/L)                  128
MINIMUM CONCENCENTRATION (MG/L)                        .937774E+01
MAXIMUM CONCENCENTRATION (MG/L)                        .111427E+02
CATEGORY        RANGE           COUNT                     PERCENTAGES
NUMBER LOW VALUE HIGH VALUE                     MEAN   BELOW WITHIN  ABOVE
------------------------------------------------------------------------------
BELOW             .9378E+01      0                              0.00 100.00
    1  .9378E+01  .9466E+01      4  .9428E+01    0.00    3.12  96.87
    2  .9466E+01  .9554E+01      3  .9518E+01    3.12    2.34  94.53
    3  .9554E+01  .9642E+01      4  .9572E+01    5.47    3.12  91.41
    4  .9642E+01  .9731E+01      4  .9707E+01    8.59    3.12  88.28
    5  .9731E+01  .9819E+01      5  .9790E+01   11.72    3.91  84.37
    6  .9819E+01  .9907E+01      7  .9869E+01   15.62    5.47  78.91
    7  .9907E+01  .9995E+01      7  .9956E+01   21.09    5.47  73.44
    8  .9995E+01  .1008E+02     10  .1005E+02   26.56    7.81  65.62
    9  .1008E+02  .1017E+02     12  .1013E+02   34.37    9.37  56.25
   10  .1017E+02  .1026E+02     12  .1022E+02   43.75    9.37  46.87
   11  .1026E+02  .1035E+02      8  .1031E+02   53.12    6.25  40.62
   12  .1035E+02  .1044E+02     14  .1040E+02   59.37   10.94  29.69
   13  .1044E+02  .1052E+02     14  .1049E+02   70.31   10.94  18.75
   14  .1052E+02  .1061E+02      9  .1057E+02   81.25    7.03  11.72
   15  .1061E+02  .1070E+02      6  .1067E+02   88.28    4.69   7.03
   16  .1070E+02  .1079E+02      1  .1079E+02   92.97     .78   6.25
   17  .1079E+02  .1088E+02      3  .1082E+02   93.75    2.34   3.91
   18  .1088E+02  .1097E+02      1  .1096E+02   96.09     .78   3.12
   19  .1097E+02  .1105E+02      1  .1100E+02   96.87     .78   2.34
   20  .1105E+02  .1114E+02      3  .1112E+02   97.66    2.34   0.00
ABOVE  .1114E+02                 0             100.00    0.00
```

Figure 1. Frequency Distribution after 128 Samples

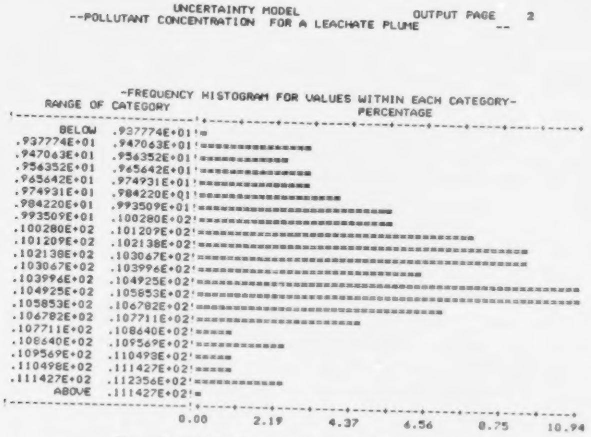

Figure 2. Relative Frequency Histogram after 128 Samples

quency histogram for concentration is approaching a normal distribution; but as shown in Figure 3, the mean and standard deviation is changing with sample size.

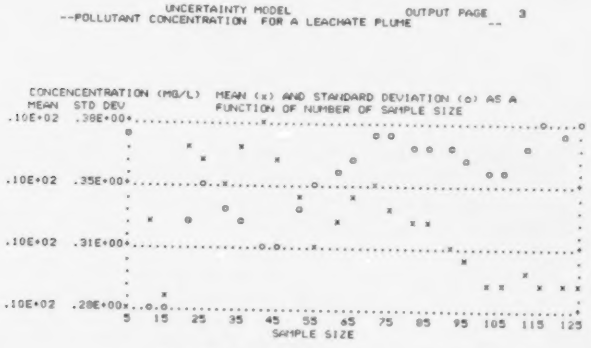

Figure 3. Mean and Standard Deviation of Concentration Distribution as a Function of Sample Size

Relative frequency histograms after a sample size of 1024 are shown in Figures 4 and 5. Note that the frequency distribution is much smoother. As shown in Figure 6. The mean and standard deviation of this distribution have become virtually independent of sample size. Thus, the sample statistics can be accepted as representing estimates of the population statistics, and the simulation was terminated. The mean of this distribution is 8.33 compared to the deterministic modeling result of 8.38.

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                  UNCERTAINTY MODEL                    OUTPUT PAGE
      --POLLUTANT CONCENTRATION  FOR A LEACHATE PLUME        4     --


SAMPLE SIZE FOR. CONCENCENTRATION (MG/L)              1024
MINIMUM CONCENCENTRATION (MG/L)                     .908976E+01
MAXIMUM CONCENCENTRATION (MG/L)                     .112646E+02
CATEGORY        RANGE        CJUNT                    PERCENTAGES
NUMBER LOW VALUE HIGH VALUE                 MEAN   BELOW WITHIN  ABOVE
-----------------------------------------------------------------------
BELOW                .9090E+01    0                        0.00 100.00
    1  .9090E+01   .9199E+01    2  .9130E+01   0.00    .20  99.80
    2  .9199E+01   .9307E+01    4  .9277E+01    .20    .39  99.41
    3  .9307E+01   .9416E+01   11  .9359E+01    .59   1.07  98.34
    4  .9416E+01   .9525E+01   20  .9465E+01   1.66   1.95  96.39
    5  .9525E+01   .9633E+01   36  .9582E+01   3.61   3.52  92.87
    6  .9633E+01   .9742E+01   49  .9693E+01   7.13   4.79  88.09
    7  .9742E+01   .9851E+01   53  .9799E+01  11.91   5.18  82.91
    8  .9851E+01   .9960E+01   70  .9905E+01  17.09   6.84  76.07
    9  .9960E+01   .1007E+02   92  .1001E+02  23.93   8.98  67.09
   10  .1007E+02   .1018E+02  108  .1012E+02  32.91  10.55  56.54
   11  .1018E+02   .1029E+02  101  .1023E+02  43.46   9.86  46.68
   12  .1029E+02   .1039E+02  112  .1034E+02  53.32  10.94  35.74
   13  .1039E+02   .1050E+02   92  .1045E+02  64.26   8.98  26.76
   14  .1050E+02   .1061E+02   98  .1056E+02  73.24   9.57  17.19
   15  .1061E+02   .1072E+02   70  .1067E+02  82.81   6.84  10.35
   16  .1072E+02   .1083E+02   45  .1078E+02  89.65   4.39   5.96
   17  .1083E+02   .1094E+02   25  .1088E+02  94.04   2.44   3.52
   18  .1094E+02   .1105E+02   21  .1099E+02  96.48   2.05   1.46
   19  .1105E+02   .1116E+02   12  .1110E+02  98.54   1.17    .29
   20  .1116E+02   .1126E+02    3  .1122E+02  99.71    .29   0.00
ABOVE  .1126E+02                0            100.00   0.00
```

Figure 4. Frequency Distribution after 1024 Samples

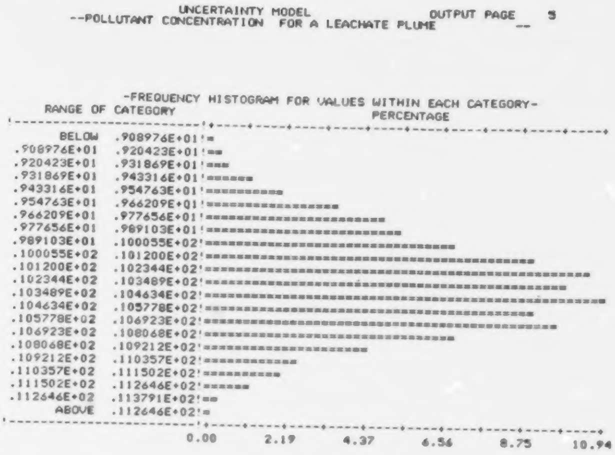


Figure 5. Relative Frequency Histogram after 1024 Samples

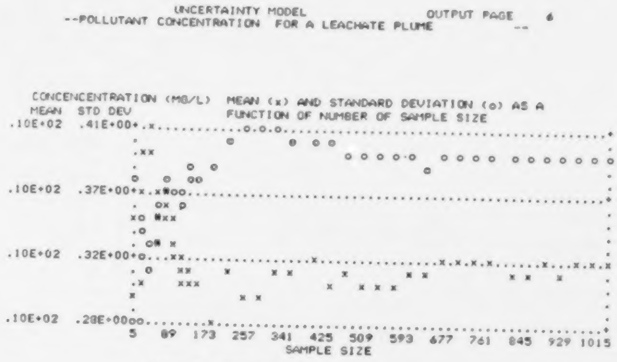
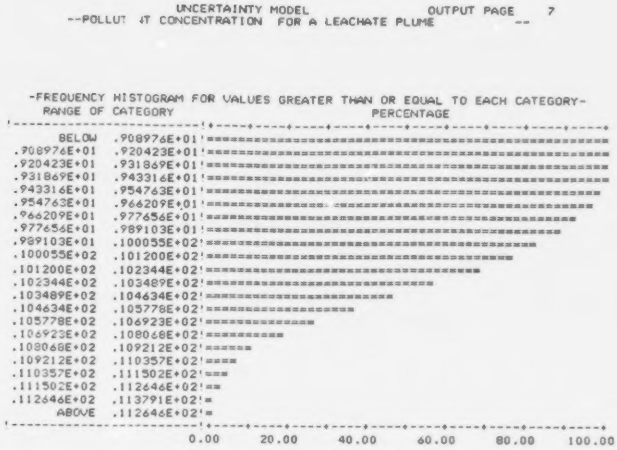


Figure 6. Mean and Standard Deviation of Concentration Distribution as a Function of Sample Size

For interpreting the results of a stochastic model in ground-water contamination studies, a cumulative frequency distribution is more useful (Figure 7). In this form, the ensemble of calculated concentrations and the corresponding probabilities can be interpreted as a risk analysis based on uncertainty in the model input parameters. In other words, there is a 50% probability that the predicted concentration is greater than or equal to 8.33 mg/l, the mean of the distribution. There is a 95% probability that the concentration is greater than or equal to 7.5 mg/l; a 5% probability that the concentration is greater than 9.0 mg/l.

In this example, the level of uncertainty, as reflected by the range of each input variable, was relatively small for a typical solute transport problem. Increasing the level of uncertainty increases both the required sample size to obtain estimates of the model output distribution statistics. The variance of the output distribution also increases, i.e., the probability density function for predicted concentrations be-



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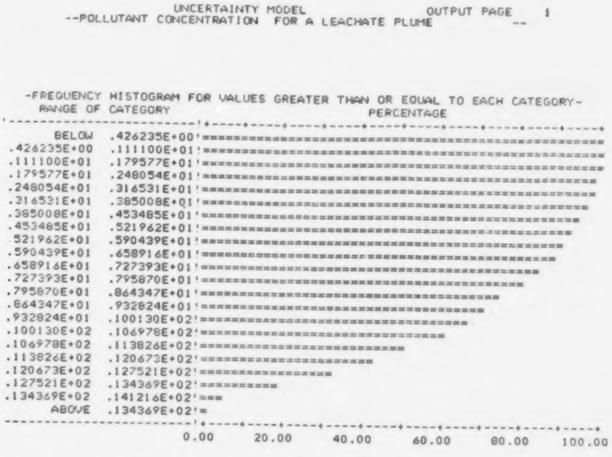
                    UNCERTAINTY MODEL                    OUTPUT PAGE    7
       --POLLUT  IT CONCENTRATION  FOR A LEACHATE PLUME              --



    -FREQUENCY HISTOGRAM FOR VALUES GREATER THAN OR EQUAL TO EACH CATEGORY-
      RANGE OF CATEGORY                                  PERCENTAGE
'------------------------!+----+----+----+----+----+----+----+----+----+----+
       BELOW   .908976E+01'==================================================
 .908976E+01   .920423E+01'==================================================
 .920423E+01   .931869E+01'==================================================
 .931869E+01   .943316E+01'==================================================
 .943316E+01   .954763E+01'=================================================
 .954763E+01   .966209E+01'================================================
 .966209E+01   .977656E+01'==============================================
 .977656E+01   .989103E+01'============================================
 .989103E+01   .100055E+02'=========================================
 .100055E+02   .101200E+02'======================================
 .101200E+02   .102344E+02'==================================
 .102344E+02   .103489E+02'============================
 .103489E+02   .104634E+02'=======================
 .104634E+02   .105778E+02'==================
 .105778E+02   .106923E+02'=============
 .106923E+02   .108068E+02'==========
 .108068E+02   .109212E+02'======
 .109212E+02   .110357E+02'====
 .110357E+02   .111502E+02'===
 .111502E+02   .112646E+02'==
 .112646E+02   .113791E+02'=
       ABOVE   .112646E+02'=
'------------------------!+----+----+----+----+----+----+----+----+----+----+
                         0.00     20.00     40.00     60.00     80.00    100.00
```

Figure 7. Cumulative Frequency Distribution for Concentration

comes wider. Figure 8 shows the cumulative frequency distribution that results from increasing the range of interstitial velocity from 1.49-1.51 to 1.0-2.0 ft/day. In this case, there is a 5% probability that the concentration will be greater than 11.3 mg/l.



```
                    UNCERTAINTY MODEL                    OUTPUT PAGE    1
       --POLLUTANT CONCENTRATION  FOR A LEACHATE PLUME               --



    -FREQUENCY HISTOGRAM FOR VALUES GREATER THAN OR EQUAL TO EACH CATEGORY-
      RANGE OF CATEGORY                                  PERCENTAGE
'------------------------!+----+----+----+----+----+----+----+----+----+----+
       BELOW   .426235E+00'==================================================
 .426235E+00   .111100E+01'==================================================
 .111100E+01   .179577E+01'==================================================
 .179577E+01   .248054E+01'=================================================
 .248054E+01   .316531E+01'=================================================
 .316531E+01   .385008E+01'================================================
 .385008E+01   .453485E+01'===============================================
 .453485E+01   .521962E+01'==============================================
  521962E+01   .590439E+01'=============================================
 .590439E+01   .658916E+01'============================================
 .658916E+01   .727393E+01'==========================================
 .727393E+01   .795870E+01'========================================
 .795870E+01   .864347E+01'=====================================
 .864347E+01   .932824E+01'===================================
 .932824E+01   .100130E+02'=================================
 .100130E+02   .106978E+02'==============================
 .106978E+02   .113826E+02'=========================
 .113826E+02   .120673E+02'=====================
 .120673E+02   .127521E+02'================
 .127521E+02   .134369E+02'==========
 .134369E+02   .141216E+02'===
       ABOVE   .134369E+02'=
-------------------------'+----+----+----+----+----+----+----+----+----+----+
                         0.00     20.00     40.00     60.00     80.00    100.00
```

Figure 8. Cumulative Frequency Distribution with a Velocity
Range of 1.0 to 2.0 feet per day

SUMMARY

Monte Carlo simulations can provide a useful means of incorporating uncertainty in model input parameters into deterministic solute transport models. The approach used in this paper neglects uncertainties in the choice of solute transport equations, but does account for uncertainties in the values of model input parameters. This, as any other stochastic modeling approach, can lead to improved decision making if properly applied and interpreted. Unfortunately, stochastic modeling studies often lead to confusion and frustration since they produce probability distributions for the model output variables rather than a single deterministic value. The additional information may be difficult to interpret and also tends to require some judgement in the decision making process. Results are no longer black and white, but rather varying shades of grey.

In this brief paper we have tried to accomplish two objectives. The first is to point out that there are uncertainties in all ground-water flow and solute-transport modeling studies. These uncertainties may arise from, among other things, uncertainties in the model to describe the physical system, and random fluctuations in the forcing functions or in the unmeasured ambient conditions affecting the process. Uncertainties may be caused by inadequate data collection techniques, including instrumentation and analysis, and uncertainties in the data used in the calculations. These stochastic features can be taken into account in deterministic models.

Secondly, the results of stochastic modeling studies can be interpreted in more familiar terms such as risk analysis. Weather forecasts have been given in these terms for several years, and we all use them to make decisions as part of everyday life. With a little effort uncertainties in ground-water modeling studies can also be included in our decision making processes, whether we explicitly use stochastic models or through an awareness of the types and sources of uncertainty in deterministic models.

ACKNOWLEDGEMENT

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SEAWATER INTRUSION IN THE SAN JUAN ISLANDS

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ABSTRACT

A study of seawater intrusion into the groundwater of three islands in San Juan County, Washington was done throughout 1980, with subsequent monitoring through summers including 1983.

The San Juan Islands possess a varying, complicated geological makeup, with strata ranging from igneous, sedimentary, both hard and loosely consolidated, as well as shales, fractured and unfractured, sand islands, moraines and eskers. The indigenous human population depends solely upon groundwater. Subsequently, hundreds of wells have been drilled which eliminated the problem of new drilling to provide water study samples. The islands also experience a well-defined, regularly occurring, well monitored wet-dry seasonal shift. These characteristics made the San Juan Islands an excellent locale to develop models of seawater intrusion.

Fifty-one in and out-of-use wells provided the sample base which were monitored monthly for possible seawater intrusion using the chloride ion concentration as an indicator. Atomic absorption was used when more detailed analyses were necessary. Data from neighboring individual wells showing seawater intrusion were used to develop a general horizontal picture of seawater intrusion patterns.

A few of the conclusions thus far are:

1. A deep well which has been drilled into fractured rock shows less variance in water composition with time. Wells drilled deep into gravels, however, show considerably more variation. As expected, the former takes much longer to recharge than the latter. There is an inverse relationship between recharge rate and degree of fracturing.
2. If a well water is to be analyzed only annually as a check against possible sea water intrusion then late fall is the best time, since water use is high, precipitation low, and the water table is lowered.
3. Physical monitoring of a well's dynamic water level is not in itself a means to be solely trusted to identify sea water intrusion since it does not always rise and fall with the tide.
4. The Ghyben-Herzberg relation which assumes simple hydrostatic conditions in a homogeneous, unconfined coastal aquifer does not describe the sea water/fresh water lens in the San Jan area studied.
5. From the year's analytical data horizontal maps delineating areas of sea water intrusion can be drawn. Vertical profile diagrams present significantly greater problems.

AREA OF STUDY

At high tide, San Juan County consists of 428 islands, approximately 175 being named, located in the northwesternmost part of the state of Washington. The islands comprise a land area of 172 square miles, or 64.9%, of the county's total area of 265 square miles.

The geology of these islands is complicated. While they are related to the surrounding mainland and Vancouver Island, they differ enough to have their own strategraphic and formational names and exhibit an amazing variety of rock types and structures. The three major continental glacial masses that advanced and retreated during the early to middle Pleistocene Epoch overrode the San Juans causing extensive erosion and deposition. As the land uplifted or rebounded above as the ice mass over 1/2 mile thick retreated, a non-marine drift consisting of sand, gravel and rocks to boulder size was deposited. Returning sea water and wave action built coastal features such as spits, tomboloes, sea cliffs and wave-cut terraces from the easily eroded sediments.

CLIMATE

Owing to the comparatively warm winds from the Pacific and their geographic position, the San Juan Islands experience mild, moderately wet winters and cool, dry summers. As is the case with the Puget Sound area, the bulk precipitation occurs during the late fall, winter and early spring, although the San Juans receive less than most of northern Puget Sound. In any "average" year 83% of the rainfall of 25" occurs from October to May (Figure 1).

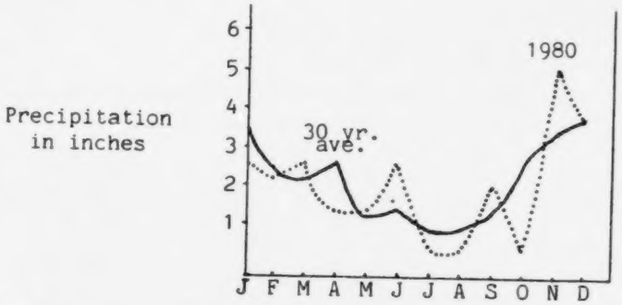

Figure 1. Total monthly precipitation for the North end of Lopez Island for 1980.

GROUNDWATER

There are no rivers or springs, some intermittent streams and only a few lakes in the San Juan Islands. Surface water quantity and quality is, in general, only fair to poor. Consequently, groundwater is the major source of water for human consumption and San Juan County is an area of major groundwater use in the state of Washington.

Unlike most areas of the mainland, west of the Cascades, the groundwater in these islands is limited. Groundwater recharge comes solely and directly from rainwater falling on the land surface and subsequent downward seepage. Much of the islands' surface is a variety of bare rock types with limited water storage capability. Additionally, a great deal of the soil mantling the bedrock is typically only a few inches thick. Subsequently, much of the rainfall in the San Juan Islands returns quickly to the sea as run-off.

The chemical characteristics of the San Juan Islands groundwater is very varied due to the large number of separate aquifers, many with varying geology. The average water hardness of the islands is about 205 ppm (very hard) with values well above and below this number (Russell, 1975).

Most of the well waters there have been sodium and chloride ion concentration. It is not always clear what the source of these ions really is for most of these well waters. The salt may be due to old deposits left as this once submerged land rose relative to sea level. This could be in the form of salt deposits (evaporites) or as trapped ancient sea (connate) water. If these are the case, as the water is used, the salt concentration should decrease due to leaching; therefore, no serious problem exists. But if salt concentration increases with time, then sea water intrusion is occurring.

THE STUDY

During an initial one year study (January 1 - December 31, 1980), the minimum time frame necessary for a wet/dry seasonal cycle, 29 previously drilled wells were monitored primarily for chloride ion. These varied in output, depth, rock type and distance from the sea but were chosen because their location made seawater intrusion a possibility. Lopez Island was selected because of potential water problems and ease of access by ferry.

All well owners and users approached agreed to the study. Each was promised and received a copy of the chloride ion annual variation with a letter of explanation for their particular well at the end of the study.

Each month a water sample was collected from each well and analyzed. The chloride ion was determined using the Knudsen Titrimetric Method at the Friday Harbor Laboratories of the University of Washington. The positive ions (sodium, calcium, magnesium and potassium) and several negative ions such as bicarbonate were measured when necessary at the Department of Aquatic Studies of Western Washington University. Most of the analyses were performed on the department's Perkin-Elmer 560 Atomic Absorption Spectrophotometer.

THE RESULTS

Seawater intrusion was found in varying degree in all of the test areas on the north end of Lopez Island (Figure 2).

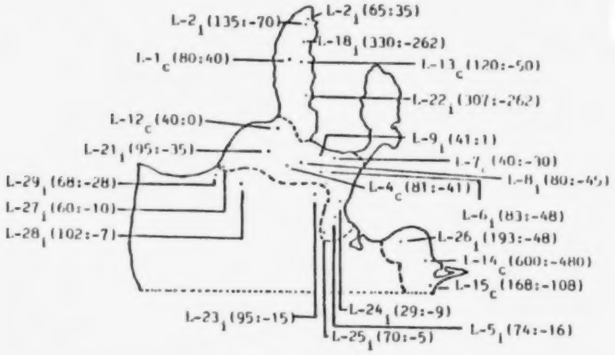

Figure 2. Study well locations with identifying code numbers, depths and distance below sea level, North Lopez Island.

The location of each well studied is given as a point along with its identifying code (i.e., L-1, L-2, etc.). The first accompanying number in parentheses represents the well depth. The second is the well's elevation above or below sea level. For example, L-4 (81: – 40) means that the well bottom is at a depth of 81 feet deep and 40 feet below sea level. All wells except two, L-15 and L-21, were in active use. The demand varied greatly from well to well since some were used by individual dwellings, others by community systems. The subscripts "i" and "c" are appended to each well code number to indicate this.

Upright Head is all bedrock composed of generally impermeable conglomerate, sandstone and shale in decreasing order of abundance but with water contained in large fracture zones. The remainder of N. Lopez is Pleisocene and recent glacial drift, till, alluvium and outwash deposits with excellent water storage capacities (McLellan, 1927; Whetten, 1975). The deep geology is not known but it isn't necessary since none of the study wells penetrate below the surface zone.

The wells on Upright Head, several of which were below sea level, showed a typical chloride concentration of between 30-40 mg/l and varied little with season (Figure 3). Deep wells in said rock show less variance in water composition with time, although Caswell (1979) found that as bedrock became more fractured it responded moderately to the tide and rainfall. Deep wells in gravels, however, show considerably more variation. Lusczynski and Swarzenski (1966), Trembly, *et al.* (1973), and Anderson and Berkebile (1976) regarded 50 mg/1 and 50 mg/1, respectively, as indicative of seawater intrusion. The wells in glacial till generally exhibited seawater intrusion. The dashed boundaried area of Figure 4 shows the limits horizontally of seawater intrusion. In this region every well shows intrusion. Some wells when first drilled encountered seawater directly; L-4, for example, at 133 feet. In the other wells seawater has been "pulled up" or upconed (Sahni, 1972) by the pumping of fresh water. By and large these wells show a seasonal variation in chloride concentration (Figure 4), the highs occurring during the period of low rainfall and high water use. It is clear that one analysis of a well's water, or even an annual analysis is not particularly indicative of the water's make-up, except at that instant, since well water composition varies drastically from time to time. This is especially true of shallow wells (i.e., less than 30 meters) (Flora, 1980). If a well water is to be analyzed annually as a check against possible sea water intrusion then late fall is the best time, since water use is high, precipitation low, and the water table is lowered.

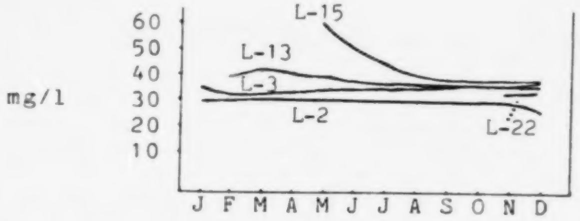

Figure 3. Variation of chloride concentration with time for wells in bedrock.

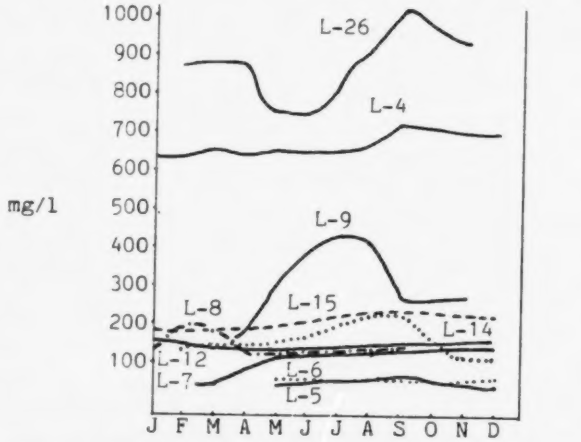

Figure 4. Variation of chloride concentration with time for wells in glacial drift.

It is generally assumed that seawater, if it exists under an island's groundwater, does so in either a lens-like or wedge configuration. The dynamic height of four wells (L-2, L-4, L-8, L-21) were physically monitored and compared with tidal fluctuations, a means for further assessing this assumption since intrusion had been chemically determined in the last three. L-2, in bedrock, showed absolutely no level change with the tide (Figure 5). Since small aquifers like these will in themselves show no tidal effects if the water level in the well fluctuates with tidal changes then it must be an indication of an underlying seawater oscillation although one has to be careful that simple barometric pressure changes or new rain groundwater recharging are not the cause. L-8 and to some small extent L-21 showed tidally related level changes. There was, however, no assessable level change as a function of well elevation absolutely or with respect to distance from the sea. L-21 is not a pumped well whereas L-8 and L-4 are. L-8 is only pumped for a single family dwelling. L-4 supplies most of the water for a system of 14 houses. L-4 showed some fluctuations but not reliably. The level changes may have been complicated by the draw

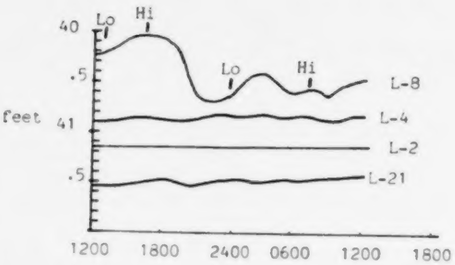

Figure 5. Well water fluctuations with time. The times of high and low tides are indicated. Tide height at the 1701 high is 7 feet, at the 0043 low is -1.0 feet.

of a well in heavy use. For L-4 the level of the seawater has been upconed by at least 40 feet. This, too, probably has its effect.

Not surprisingly, data suggest all of the north end of Lopez is underlain with seawater. Wherever a well was drilled deep or pumped hard intrusion occurs. The seawater cannot be moving horizontally since a number of wells further from the sea often exhibited intrusion whereas ones of the same depth between these intruded wells and the sea did not. Patterns of intrusion also show that upconing is very localized (Figure 4).

Ghyben (1889) and Herzberg (1901) determined independently that static seawater existing underground below unconfined coastal aquifers was not at sea level but at a depth below sea level 40 times the height of the fresh water lens above sea level. This apparently does not describe the situation on Lopez. At L-4, for example, ground water was found at 30', 10' above sea level. Sea water should have been found at 400' instead of at 133'. In all probability this unconfined aquifer, horizontally and vertically permeable, is too thin to be described by Ghyben-Herzberg. A more realistic empirical value for this area (with an average lens thickness of 100') is a ratio of 10-13 to 1.

While most model studies of seawater (i.e., salt water) intrusion have assumed a variety of other conditions, a sharp boundary between sea and groundwaters was commonly held (Ghyben, 1889; Herzberg, 1901; Glover, 1959; Rumer and Harleman, 1963; Bear and Dagan, 1964; Rumer and Shiau, 1968; Van der Veer, 1977). The exception was Henry (1964). Considering that the fresh water of river discharges can be found at sea miles off of a coast floating unmixed on seawater and that the seawater pumped directly from some of the study wells has a chloride concentration of approximately 19,000 mg/l whereas the water of the intruded wells was almost always much less than 1000 mg/l, there is not much prediliction toward mixing. This boundary condition would be called a halocline or pyknocline by an oceanographer. Any slight lack of sharpness, or apparent sponginess, to the boundary may be due to a slight mixing action interstitially in the sand and gravels caused by the tides, mentioned as early as 1933 (Riddel).

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SUBSURFACE TRANSPORT OF URBAN RUNOFF POLLUTANTS

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ABSTRACT

Five injection tests were conducted on an experimental dry well at a site near Tucson, Arizona. Primary goals of the tests were to determine flow patterns in the vadose zone, and attenuation of urban runoff pollutant analogs (metal, microorganisms, and organic matter) in vadose zone/groundwater flow systems. A perched ground-water system and a water table mound were observed by neutron moisture logging with lateral flow velocities averaging 500 ft/day. Metals were detected breaking through in a vadose-zone sampling well. Microbial tracers were also observed in the vadose zone sampling wells, but peak values were markedly reduced below input values. The initial concentration of organic matter breaking through in the sampling well was 58% of the input values. No organic matter of microorganisms were detected in pumped ground-water samples. It was generally concluded that (1) dry well injection of urban runoff may develop perched ground-water systems capable of spreading injected water within the radius of influence of nearby wells, and (2) given the pollutant loading rates of the test, ground water was not deteriorated in quality.

INTRODUCTION

Many communities in Arizona require developers to provide detention/retention schemes to prevent flooding of downstreams areas as a result of increased runoff from their projects. The most commonly employed technique for on-site retention of flood waters is the so-called "dry well". By definition, a dry well is a structure which facilitates the rapid movement of flood water into permeable vadose zone sediments. Currently, there are more than 6000 operating dry wells in Arizona, with the largest concentration being in the Phoenix area.

Although dry wells are highly effective for disposing of flood water, there is concern that pollutants in runoff water may eventually degrade underlying ground water. Based on the results of urban runoff studies in Fresno (Brown and Caldwell, 1982), it appears that the principal pollutants from runoff in semiarid regions include heavy metals, microorganisms, and organic substances. So far, information on the fate of pollutants in the vadose zone and ground-water systems during dry-well disposition of runoff is lacking. Five injection tests were conducted on an experimental dry well at a site near Tucson, Arizona. The main purpose of the tests was to evaluate the extent that pollutants in urban runoff are attenuated during lateral and vertical flow in the vadose zone and during mixing with ground water. An additional goal was to characterize flow patterns and velocity of dry well injected water in the vadose zone.

METHODOLOGY

The experimental well is a compartmentalized type commonly used for disposal of urban runoff in several Arizona communities (McGuckin 1981). The upper chamber consists of a six-foot diameter concrete-pipe settling chamber, with an overflow pipe extending into the bottom compartment. The bottom compartment is a gravel-packed, four-foot diameter shaft, extending from 12 feet to 23.5 feet below land surface. The shaft contains a connecting pipe to the overflow pipe from the upper chamber. The basal region of the shaft terminates in coarse vadose-zone sediments. The water table at the site is about 110 feet below land surface. Consequently, approximately 86 feet of vadose-zone sediments are available for vertical filtration of injected water. Horizontal filtration also occurs during lateral flow in perched ground-water systems.

The well is located in the midst of an extensive monitoring well network, including 100 feet deep access wells for neutron moisture logging, depth-wise water sampling wells in the vadose zone, observation wells, and a 300 foot deep pumping well. Water sources for testing include irrigation water and pumped ground water. The hydrogeology at the site has been characterized during previous experiments.

The tracers which were injected into the water source to simulate urban runoff pollutants and the associated tests were as follows:

(1) metals (iron, copper, zinc), test 1;
(2) microorganisms (*E-Coli*, Fecal Streptococci, and f2, a bacteriophage), tests 2, 3, and 4; and
(3) organic matter, microorganisms (*E-Coli*, Fecal Streptococci), nitrogen species, test 5.

Input tracer concentrations are summarized in Table 1. The metals and microorganisms were injected as slugs several hours after the beginning of each test, i.e., after the perched system became fully developed. During test 5, the organic matter and other pollutants were injected into the well at the start of the test to simulate the "first flush" of pollutant-laden urban runoff. The inflow rates of water during the tests ranged from 500 gpm for the first test to 200 gpm in the fifth test. Rates averaged about 280 gpm for the second, third and fourth tests. Rates were held steady during each test. The duration of each test was about 10 hours.

TABLE 1
Average Concentatrations of Pollutant Tracers
and
Injected Into Dry Well During
The First Four Tests

TEST NUMBER	DURATION OF INJECTION (HRS.)	MICROORGANISMS			METALS		
		E-Coli (no./100mls)	Fecal Strep. (no./100mls)	f2 (no./100mls)	Iron (mg/ℓ)	Copper (mg/ℓ)	Zinc (mg/ℓ)
1	0.92	-	-	-	6.52	0.15	0.5
2	0.62	1.105×10^5	3.22×10^4	6.3×10^3	-	-	-
3	0.50	2.82×10^4	-	197	-	-	-
4	0.62	1.5×10^3	2.31×10^3	2.7×10^3	-	-	-

TABLE 1b
Average Input Concentrations of Pollutant
Tracers During Test Number 5

DURATION OF INJECTION (HRS.)	NITROGEN SERIES				MICROORGANISMS		ORGANICS	CONSERVATIVE TRACER
	NH_4-N (mg/ℓ)	NO_3-N (mg/ℓ)	ORG-N (mg/ℓ)	Total N (mg/ℓ)	E-Coli (no./100mls)	Fecal Strep. (no./100mls)	TOC (mg/ℓ)	Chloride (mg/ℓ)
1.2	5.6	0.9	0.6	7.1	27	443	45.4	325

During injection, water samples were collected at the dry well to characterize input concentrations of the tracers. Perched ground-water samples were available only from a 25 foot deep well 49 feet from the injection well and from an observation well with cascading water, 88 feet from the well. These samples were used to characterize the effects of lateral flow on pollutant transport. Metals were quantified using an atomic absorption spectrophotometer. The microorganisms were assayed in an on-campus laboratory. Organic matter was characterized as TOC.

Survival experiments were conducted on microorganisms during test 2, 3, and 4. The procedures for these tests were presented in Wilson (1983). During test 2, *E-Coli* and fecal streptococci organisms did not survive beyond two hours. In contrast, large concentrations of the *E-Coli* bacteria survived during the viability tests for test 3 and 4. Following the completion of test 5, the water supply well was pumped for a brief period each day for five days, and samples were taken for analysis of each of the tracers. One week after the test, a 24 hour pumping cycle was initiated and water samples were obtained for analysis of the tracers every hour.

Water content changes in the layered vadose-zone sediments were monitored during the first two injection tests by neutron moisture logging in access wells.

RESULTS AND DISCUSSION

Neutron moisture logs depicted two nearly-saturated regions in the vadose zone during dry-well injection. The uppermost region is perched ground water and the lowermost region is a mound overlying the water table. Apparently, lateral flow from the well creates the perched region and vertical leakage from the perched system generates the water table mound. The region between the two zones transmits water without a change in water content. Using the neutron moisture logs, the laterial flow velocity of perched ground water was estimated to vary from 260 ft/day to 750 ft/day. The vadose-zone flow system quickly spread to a region encompassing the cone of depression of the pumping well.

Metals

The breakthrough curves for the metals during the first test indicated that these tracers arrived in the 25 foot well in pulses, apparently because of variations in flow paths (dispersion) and physical-chemical reactions. The maximum relative concentrations of iron and copper detected in the well were 40 percent and 20 percent, respectively.

Biological Tracers

In view of the very poor survival rate of the three microbial tracers during the second test, results from this test are omitted in our discussion. Breakthrough patterns and relative masses of tracers for the other tests are discussed. Breakthrough patterns are useful for evaluating the relative arrival times, flow velocities, and flow patterns of the tracers. Breakthrough curves of microbial tracers at well 1 and well 2 during test 3 are depicted on Figures 1 and 2, respectively. From Figure 1, it appears that coliform arrived first at well 1 during test 3. This result is unexpected in that one would expect that greater filtration of the rod-shaped coliform would retard flow velocities compared with the smaller bacteriophage. Fluctuations are apparent in both the *E-Coli* and f2 curves, particularly after an initial peak between 1 and 2 hours. These fluctuations may represent variations in flow patterns and attenuation processes. Inasmuch as the curves are in rough correspondence, attenuation processes are possibly similar for the microorganism. For these tests, dilution, filtration and vertical drainage are probably the major attenuation mechanisms. The relative values of f2 were generally greater than those for coliform. The curves for the cascading well, about 40 feet further from the dry well than the 25 ft. sampling well, also depict fluctuations in the arrival of tracers. The C/C_0 values were lower than corresponding values in the 25 foot well, indicating additional attenuation with distance from the source. The coliform peak occurred about 3 1/2 hours after beginning the test. Later f2 values oscillated between zero and finite values.

FIGURE 1. Breakthrough Curves for Microbial Tracers, Test Number 3, Well Number 1.

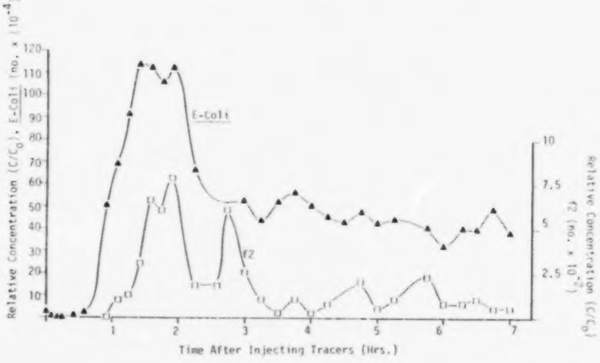
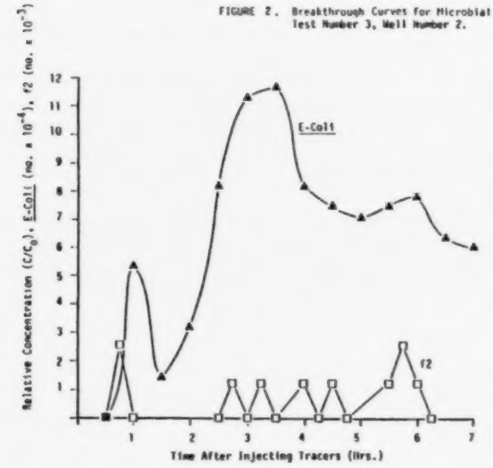


FIGURE 2. Breakthrough Curves for Microbial Tracers, Test Number 3, Well Number 2.



During the fourth test, f2 failed to arrive in well 1. As shown on Figure 3, a prolonged breakthrough in *E-Coli* occurred in contrast to the abrupt breakthrough of fecal streptococci. Again, this result is contrary to expectations in that one would expect the rod-shaped coliform to be more retarded than the spherical fecal streptococci and smaller f2 particles. The breakthrough curves for coliform and f2 in well 2, are relatively uniformly-shaped, with only slight oscillations, indicating that flow/attenuation processes were at a relatively steady state during the fourth test. Fecal streptococci organisms were absent from cascading well samples. Inasmuch as the survival rates of all three organisms were uniformly high, it appears that attenuation processes in the vadose zone effectively removed fecal streptococci from the flow stream. In contrast to the absence of f2 at well 1 (see Figure 4) a dis-

FIGURE 3. Breakthrough Curves for Microbial Tracers, Test Number 4, Well Number 1.

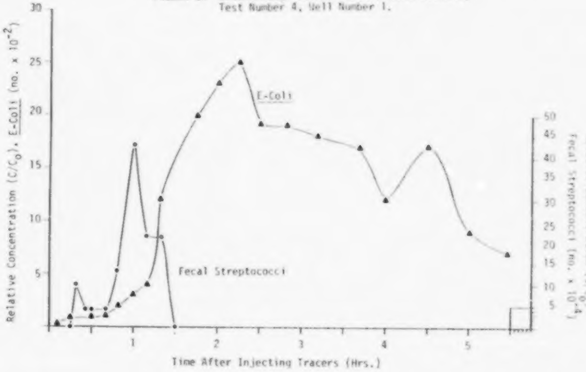
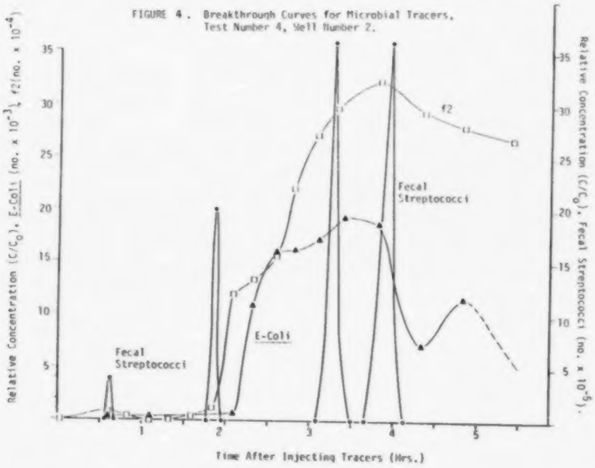


FIGURE 4. Breakthrough Curves for Microbial Tracers, Test Number 4, Well Number 2.



tinct breakthrough of the bacteriophage occurred at well 2. These results suggest that attenuation processes inhibited the flow of f2 toward well 1 during this test and that such processes were less restrictive in a flow direction oriented toward well 2. As expected, the breakthrough for coliform and fecal streptococci in well 2 during test 4 lagged behind the curves for well 1, and further attenuation occurred between the wells.

Velocity values calculated from the breakthrough curves were within the range of the value 750 ft/day obtained by neutron logging. In other words, microorganisms are rapidly transmitted through the perching layer to a region above the cone of depression of the nearby pumping well.

The fraction R of tracer arriving at a sampling point cannot be determined quantitatively because of leakage from the perching layer during flow. However, an idea of the relative masses passing the sampling point can be obtained by comparing areas under the various C/C_0 versus $t/\Delta t$ curves (Δt = total time that a tracer is injected). (Details of the method are discussed by Wilson, 1983.) If there are no sources in the flow system, the relative mass value will be less than unity and the smaller the value the greater the attenuation. This approach thus allows us to estimate the relative attenuation of the various tracers.

Each of the breakthrough curves for the three tracers were replotted as C/C_0 vs. $t/\Delta t$. (These curves are not included.) To facilitate comparing results between tests of different duration, the time period selected for integration of the curves was 5.5 hours. The area was determined by planimetering. Results of the relative mass estimates are summarized in Table 2. Inasmuch as the values are all less than unity, it appears that there were no sources of tracers, i.e., attenuation exceeded augmentation.

TABLE 2

Relative Masses of Tracers Estimated from Breakthrough Curves

Well Number 1

Test Number	E-Coli	Fecal Streptococci	f2
3	5.69×10^{-2}	-	0.38
4	0.82	2.8×10^{-3}	0

Well Number 2

Test Number	E Coli	Fecal Streptococci	f2
3	6.84×10^{-3}	-	5.13×10^{-3}
4	0.72	0	1.5×10^{-2}

In general, the relative mass (RM) of *E-Coli* exceeded that of either fecal treptococci or f2, the exceptions being test 3 at well 1 when the relative mass of f2 exceeded that for *E-Coli*. These results suggest that attenuation processes were generally not as important for reducing overall E-*Coli* masses as for the other tracers. Observe, however, that the RM values of *E-Coli* during test 4 at both wells were much greater than the corresponding values during test 3 suggesting that attenuation was less during test 4. Also, the coliform RM value for well 2 remained fairly high (i.e., 0.72 vs. 0.82 in well 1), implying that although the relative concentrations of coliform were reduced during additional flow to well 2, the overall masses were about the same.

The RM values in well 1 for fecal streptococci were much less than the associated values for *E-Coli* and f2. Thus, loss factors were more effective in reducing fecal streptococci during flow between the dry well and well 1. The RM value was reduced to zero during further transit to well 2.

The fairly large RM value for f2, namely 0.38, determined for well 1 during the third test implies that attenuation was less during this test. The RM values for the bacteriophage decreased between wells 1 and 2, except for test 4, when a value of 0 was determined for well 1 c.f. 1.5×10^{-10} for well 2. These results seem to imply that either the attenuation processes or flow paths for f2 vary from test to test.

Organics

Fairly high concentrations of TOC were detected in the first sample from the 25 foot well during the fifth test. In other words, attenuation processes operating during lateral flow in the vadose zone were not effective in preventing the migration of organics. A decrease in TOC in later samples indicated that dilution was effective as an attenuation process. Following the test, the nearby 300 foot well was pumped periodically for about a week. Then a 24 hour pump test was conducted. No trace of TOC was detected in pumped samples. Thus, vertical filtration of the injected water through 80 feet of vadose-zone sediments, coupled with mixing below the water table completely reduced organic matter below detectable limits. Coliform and fecal streptococci organisms were also completely absent from ground-water samples.

CONCLUSIONS

The following conclusions apply to hydrological conditions similar to those at the site of the experimental dry well.

(1) Dry well injected water may create one or more perched groundwater systems. The lateral velocity of water in these systems may be quite high, transporting pollutant-laden water to within the cone of influence of nearby pumping wells.

(2) Heavy metals may not be completely attenuated during lateral flow in the vadose zone.

(3) Microorganisms are drastically reduced in concentration during lateral flow in the vadose zone, ostensibly because of dilution, filtration, and vertical drainage from the perched layer. Velocities of microorganisms in the perched system approach the rate of water movement as observed by neutron moisture logging.

(4) The order of attenuation appears to be fecal streptococci > f2 > *E-Coli*.

(5) Attenuation processes may not be completely effective in reducing peak organic matter concentrations in dry-well injected water during lateral flow in the vadose zone. However, vertical filtration through the vadose zone coupled with mixing below the water table may reduce organic levels to below detection limits.

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FINITE ELEMENT METHOD WITH REGION WISE ITERATION SCHEME FOR SOLVING GROUNDWATER SOLUTE TRANSPORT EQUATION

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ABSTRACT

By using subregion iteration with the orthogonal weighting finite element method for the computations of large-field problems of groundwater solute transport, the CPU memory requirement can be drastically reduced. The convergence rate is enhanced over the pointwise iteration method. The use of orthogonal weighting functions assures the convergence because the resulting coefficient matrix is always irreducible and diagonally dominant. Such properties of a matrix are closely tied to the sufficient conditions for the convergence of an iteration method.

Computer runs for test problems were carried out for 10 x 10, 30 x 30 and 50 x 50 grid systems with 2, 3 and 4 subregions. The CPU memory and CPU time were monitored during each run. The numbers of iterations required for the convergence in each time step were also recorded. The results are useful information for the determination of the number of subregion required for a given computer memory capacity and for the estimation of the CPU time using the subregion iteration method.

INTRODUCTION

The Galerkin finite element has been used extensively to solve groundwater flow and solute transport problems (Pinder and Gray, 1977, Yeh and Ward, 1981). When large-field problems are to be dealt with, employing the direct elimination method to solve the finite element equations becomes impractical because of excessive requirement for CPU memory. For example, a 100 x 100 node discretization for two-dimensional case of a 100 x 100 x 10 node discretization for three-dimensional solute transport computation, will require more than 16 megabytes of computer storage for the banded coefficients matrix alone. An IBM 370/3033 main frame computer which has 18 megabytes of CPU memory can barely handle this case.

If pointwise iteration of Galerkin finite element methods is used to solve such matrix equations instead of a direct elimination method, the tradeoff is longer computing time for excessive CPU memory requirement. Not only is the convergence rate rather slow for pointwise iteration, it has also been shown that an ill-conditioned matrix is often encountered for anisotropic media, resulting in nonconvergence for the pointwise iteration of Galerkin finite element methods (Yeh, 1983).

Convergence of the point iterative scheme is closely tied to the irreducibility and diagonal dominance of the coefficient matrix in the finite element method (Pinder and Gray, 1977). The orthogonal weighting finite element scheme which was first introduced by Yeh (1983) can generate a well-conditioned coefficient matrix with desired properties such as diagonal dominance and irreducibility and, therefore, provides the sufficient conditions for the convergent solutions of pointwise iteration method. The sufficient conditions are also applied to the convergence of block iteration method (Forsythe and Wasow, 1969, Westlake, 1968).

In this paper the discretization for the two-dimensional large-field problems are further divided into subregions. Finite element formulations are written for each subregion. The formulations for the subregions are related through the imposition of the Dirichlet boundary conditions on the interboundary lines. The computations start from one subregion at one end of the solution domain marching down to the other end. A sequence of such computations completes one iteration. Since the CPU memory for only a single subregion is needed for the banded coefficient matrix, the overall memory requirement is drastically reduced provided the nodal points for each subregion are properly numbered. Also, for the reasons mentioned earlier, the orthogonal weighting scheme was employed for the assurance of convergent solutions. Thus, the subregion iteration method presented herein is equivalent to the convergent block iteration method. The convergence behavior of subregion iteration method for a number of grid systems of various size was examined. The results will be presented in the later sections.

THE ORTHOGONAL WEIGHTING FUNCTIONS

The conventional Galerkin finite element method uses the interpolation function itself as the weighting function. But the orthogonal weighting finite element scheme has the weighting functions so chosen that the resultant matrix is irreducible and diagonally dominant thus satisfying the sufficient conditions for the convergent point or block iteration solutions (Pinder and Gray, 1977).

For a linear quadrilateral element the interpolation functions of typical element are (Becker, et al., 1981):

$$N_1 = (1-\xi)\,(1-\eta)/4$$

$$N_2 = (1+\xi)\,(1-\eta)/4$$

$$N_3 = (1+\xi)\,(1+\eta)/4$$

$$N_4 = (1-\xi)\,(1+\eta)/4$$

and the orthogonal weighting functions are (Yeh, 1983):

$$W_1 = (1-6\xi+5\xi^3)\,(1-6\eta+5\eta^3)/4$$

$$W_2 = (1+6\xi-5\eta^3)\,(1-6\eta+5\eta^3)/4$$

$$W_3 = (1+6\xi-5\xi^3)\,(1+6\eta-5\eta^3)/4$$

$$W_4 = (1-6\xi+5\xi^3)\,(1+6\eta-5\eta^3)/4$$

The derivation of the orthogonal weighting functions and the need of using the orthogonal weighting function for groundwater flow problems in anisotropic media demonstrated in the author's earlier paper (Yeh, 1983).

In the groundwater solute transport computation the dispersion coefficients are modeled as functions of the longitudinal and transverse dispersivities and the velocity components as presented by Scheidegger (1961). It is known that any differences in the transverse and longitudinal dispersivity and/or in the x- and y-velocity component will result in anisotropy of dispersion coefficients. Thus, for a guaranteed convergence of iterative computation of finite element method, orthogonal weighting schemes should be used.

SUBREGION AND NODAL NUMBERING SYSTEM

The band width of the matrices in the finite element formulas can be reduced if proper nodal numbering system is used. In general, the nodes should be numbered in sequence along the short side (the side with less number of nodes) and marching down along the long side line by line.

A 10 x 10 grid system is shown in Figure 1. The nodal numbers as well as the element numbers of the global system are indicated in the figure. The CPU memory requirement of direct elimination method for the banded coefficient matrix is 8 x (2m + 1) x n bytes. Here, n is the total number of nodes, (2m + 1) is the band width (m being the maximum difference of any two node numbers in an element) and 8 bytes are occupied per each double precision real number. For a 10 x 10 grid, m = 11, n = 100 and 8 x (2m + 1) x n = 18.4 K-bytes. But for a 100 x 100 grid, m = 101, n = 10,000 and CPU memory requirement = 16.2 megabytes. For an even larger grid system it becomes

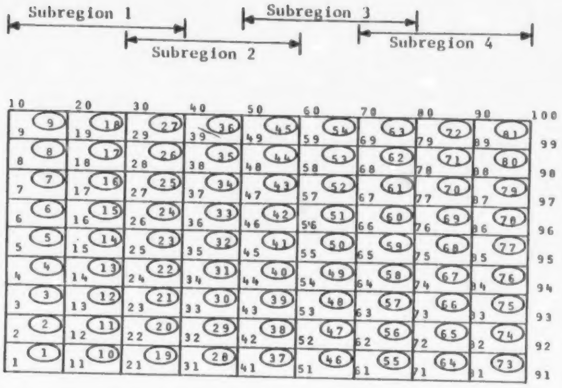

Figure 1 The global nodal numbers and elements

impractical because of excessive memory storage required. However, if the global grid system is divided, for example, into 4 subregions as shown in Figures 1 and 2, for each subregion m = 4, n = 30 and CPU memory = 2.16 K-bytes. Similarly, in each of the 10 subregions of 100 x 100 node discretization, m = 11, n = 1000 and CPU memory 184 K-byte. Such CPU memory requirement is accessible to personal computers!

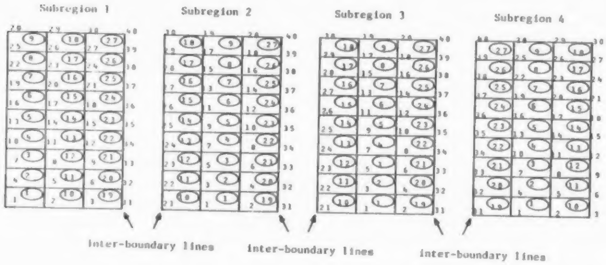

Figure 2 The subregion nodal numbers and elements

Note that the nodal numbering system is changed in the subregion in order to achieve minimum m. In counting m, the nodes on the inter-boundary lines are excluded because Dirichlet boundary conditions are imposed on these lines. The nodal unknowns on these lines can be eliminated through the matrix partitioning techniques before the execution of direct elimination of the banded matrix (Desai, 1979).

The CPU memory requirements for various grid systems (Pinder and Gray, 1977) are shown in Figure 3. The memory requirement reduces drastically as the number of subregion increases.

The computer programming for the subregion iteraction finite element method is rather straight forward because the finite element formulation for the subregion is identical to that for the global region. However, the Dirichlet boundary condition is applied to the inter-boundary lines on which the nodal values of the previous time step are assumed. In each time step, the residue of the k-th node at the i-th iteration is defined as

$$\text{Residue} = \left|\frac{C_k^i - C_k^{i-1}}{C_k^i}\right|$$

When the maximum residue is less than 10^{-4}, the solute concentration obtained is regarded as convergent solution for that particular time step.

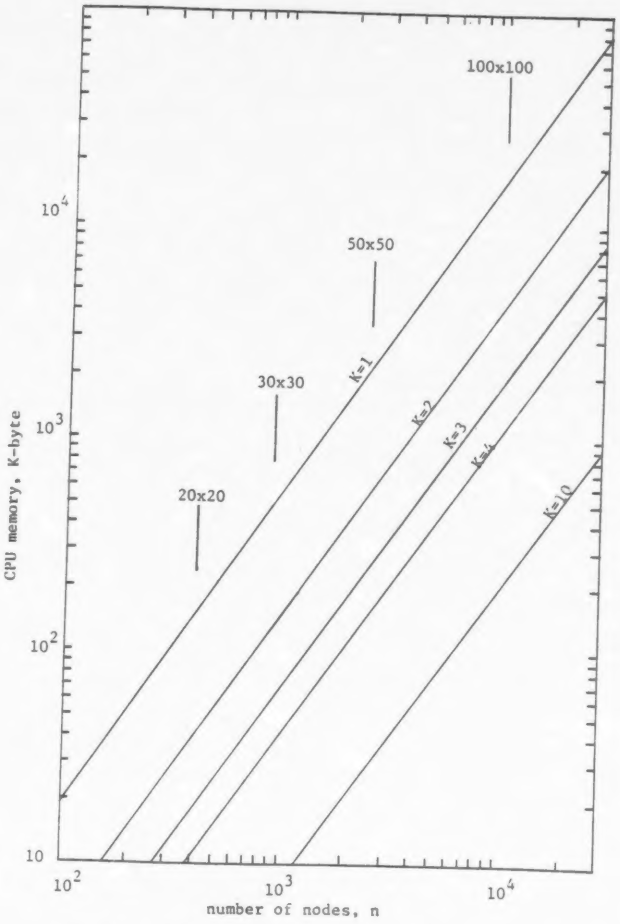

Figure 3. The CPU memory requirement for various numbers of subregions

The computer codes used here is a modified version of FEMWASTE (Yeh and Ward, 1981). The orthogonal weighting was introduced and the relationship between the local subregion nodal numbers and the global nodal numbers was implemented in the computer program.

RESULTS AND DISCUSSION

Computer runs were carried out for a test problem using four grid systems: 10 x 10, 20 x 20, 30 x 30 and 50 x 50. Each grid system was further divided into 2, 3 and 4 subregions.

The test problem is a computation of groundwater solute concentration distribution in a rectangular domain of 548.6 x 274.3 m. A Gaussian line source is located along the west boundary and centered at (x = 0, y = 121.9) for simulating a constant emission of leachate from a landfill. The same test problem was used by Gureghian, et al. (1980) for the accuracy of various finite element scheme. The governing equation is

$$\frac{\partial c}{\partial t} = D_{xx}\frac{\partial^2 c}{\partial x^2} + D_{yy}\frac{\partial^2 c}{\partial y^2} - V_x\frac{\partial c}{\partial x} - V_y\frac{\partial c}{\partial y}$$

The initial and the boundary conditions are

$$c(x,y,0) = 0 \qquad 0 \leq x \leq 548.6;\quad 0 \leq y \leq 274.3$$

$$c(0,y,5) = \exp\,[-(y-121.9)^2/(3140.1)] \quad \text{for } x = 0;\quad 0 \leq y \leq 274.3$$

$$\bar{\bar{D}} \cdot \nabla \cdot \vec{n} = 0 \quad \text{on } y = 0; \qquad 0 \leq x \leq 548.6$$

$$y = 274.3; \qquad 0 \leq y \leq 548.6$$

$$x = 548.6; \qquad 0 \leq y \leq 274.3$$

$D_{xx} = 7.432$ m^2/day, $D_{yy} = 0.020$ m^2/day, $V_x = 1.219$ day and $V_y = 0.305$ m/day. The initial time step is 1 day. The time step then increases above its former value by a factor of 1.2 at every time step until an upper limit of 25 days is reached. The computed concentration distribution at 175 days compared well with the analytic solution (Cleary, 1978).

The computations were executed using VAX 11/750 computer and the CPU time was monitored after the completion of each iteration. It was anticipated that a major portion of the CPU time would be spent to decompose the banded coefficient matrix. The decomposition requires $n^3/3$ operations for a full matrix and nm^2 operations for a banded matrix (Pinder and Gray, 1977). Obviously, the CPU time would be proportional to nm^2. In Figure 4 CPU time is plotted against nm^2 in a log-log paper and an approximate linear relationship is clearly suggested.

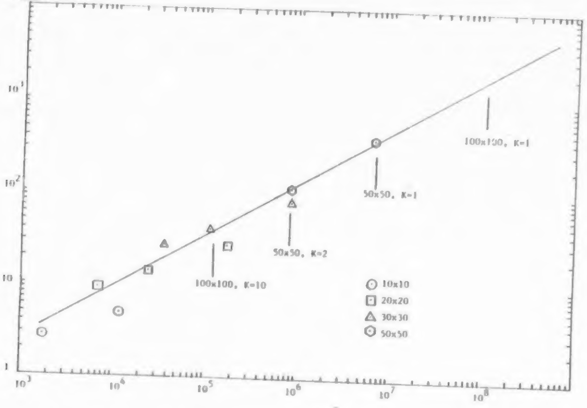

Figure 4 The relationship between CPU time and nm^2

The number of iteration for each time step of computation decreased as the number of time steps progressed. The results of two typical cases 10 x 10, 4 subregions and 20 x 20, 2 subregions are presented in Figure 5. At time step 20 the number of iteration for a converged solution is less than 40 for all cases. The numbers of iteration for the initial time steps are larger if it is divided into more subregions. For same number of subregions the number of interaction for the initial time step is slightly larger for a bigger grid system.

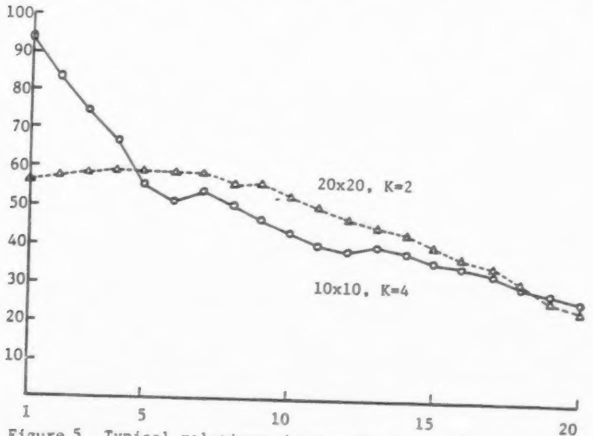

Figure 5 Typical relations showing the decreasing trend of number of iteration for each time step

For a 100 x 100 grid system the CPU memory requirement and computing time can be estimated from Figure 4 and 5. Without iteration (K = 1) CPU memory requirement is at least 16.24 megabytes with CPU time of around 1800 sec. for each time step computation. With 10 subregions, it will need about 124 K CPU memory with a CPU time estimated to be 1600 sec. (taking an average of 40 iterations for each time step).

CONCLUSIONS

In dealing with large-field problems of groundwater solute transport the Galerkin Finite element method becomes impractical because of excessive CPU memory requirement. Most computers, (for example, the IBM 370/3033 having main frame 18 megabyte CPU memory) cannot be used to handle node discretization larger than 100 x 100. The difficulty of excessive storage can be resolved by using the pointwise iteration scheme of the Galerkin method but the rate of convergence is slow. Furthermore, an ill-conditioned matrix is often encountered for anisotropic media or nonsquare discretization of isotropic media, and resulting in nonconvergence. With the employment of the subregion iteration of orthogonal finite element scheme proposed in this paper for two-dimensional discretization with quadrilateral elements, it has been shown that the memory requirement is reduced, the convergence rate is enhanced over the pointwise iteration and the coefficient matrix is always irreducible and diagonal dominant which are desired properties of the coefficient matrix for convergence.

The finite element formulation for each subregion is the same as that for the whole region except that on the inter-boundary lines for each subregion the Dirichlet boundary conditions are applied using the nodal values of the previous time step. The nodal numbering system for the subregion was illustrated to obtain the smallest m (2m + 1 being the band width) for CPU memory reduction.

The CPU memory requirement is 8 x (2m + 1) x n, n being the number of total nodes in a subregion. The memory requirement in terms of K-byte as function of node discretization for various number of subregions are plotted in Figure 3. The CPU time was monitored during the computerization of a test problem with grid systems of 10 x 10, 20 x 20, 30 x 30 and 50 x 50 for 2, 3 or 4 subregions. The CPU time was found to be linear proportional to nm^2 as shown in Figure 4.

The number of iteration for a convergent solution for each time step decreases in the later time steps. An average of 40 iterations at the twentieth time step was observed. For any node discretization of this domain other than the ones used here, the number of subregions required for a computer of a given CPU memory can be determined through Fig. 3 and the CPU time can be estimated through the use of Fig. 4.

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INVESTIGATIVE
METHODOLOGY FOR PROCESS RESEARCH

SOME CONCEPTS PERTAINING TO INVESTIGATIVE METHODOLOGY FOR SUBSURFACE PROCESS RESEARCH

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ABSTRACT

Problems of investigative methodology comprise a critical and often preponderant element of research to delineate and quantitate processes which govern the transport and fate of pollutants in subsurface environments. Examination of several recent research studies illustrates that both laboratory and field (in-situ) methodologies are useful in subsurface processes research, but also clearly shows that such research involves formidable methodological problems which result primarily from the nature of terrestrial subsurface environments. Such environments are usually remote and relatively inaccessible. This causes major methodological problems in acquiring authentic, uncontaminated samples of water and/or solids for analysis and microcosm construction. Subsurface environments are also highly structured and often exhibit significant heterogeneity across relatively short distances, which causes difficulties in determining proper locations for sample acquisitions and in simulating subsurface environments in the laboratory. Finally, slow rates of movement and long residence times of water and pollutants within subsurface environments are responsible for methodological problems associated with the need to detect and characterize processes occurring at very slow rates. Advances in a number of diverse areas, including particularly geophysical methods, analytical procedures, microcosm technology, and drilling, coring, and well completion techniques, are required for needed improvements in methodology for subsurface processes research.

INTRODUCTION

When public concern regarding environmental pollution began to be translated into action in the U.S. during the early 1960's, relatively extensive efforts directed toward protection of the quality of air and surface water resources were initiated. The ground water resource, however, remained largely out of sight and out of mind, with only a very few scientists and engineers voicing concern that human activities might adversely affect ground-water quality. Within the past few years, this concern has been vindicated, as it has become quite clear that pollution of ground water is a major environmental problem that must be addressed if the quality of this valuable and irreplacable resource is to be protected from serious degradation. At the same time, it has become equally apparent that effective and economical protection of ground water quality is likely to be achieved only if it is based on definitive knowledge of the transport and fate of pollutants in the subsurface, including both the unsaturated soil profile and underlying saturated formations. Consequently, research to delineate and quantitate the processes which govern the transport and fate of pollutants in subsurface environments is of paramount importance in providing the scientific base required for effective control of ground-water pollution.

As in any scientific endeavor, progress in environmental processes research is dependant on the development and application of methodology appropriate for investigation of the phenomena of interest. Investigations of processes which govern transport and fate of pollutants in the terrestrial subsurface involve especially formidable problems in methodology, primarily because of the relative remoteness and highly structured nature of the environments in which these processes occur. Consequently, problems of investigative methodology comprise a critical and often preponderant element of research pertaining to subsurface transport and fate processes, and these problems must be effectively addressed if such research is to be successful.

This paper discusses three relatively recent research studies pertaining to the transport and fate of pollutants in subsurface environments which are illustrative both of methodological concepts useful for investigating subsurface processes and of inadequacies and problems of such methodologies.

STUDIES ILLUSTRATIVE OF METHODOLOGIES FOR INVESTIGATING SUBSURFACE PROCESSES

Biotransformation Studies Employing Small-Scale Laboratory Microcosms

Wilson et al. (1983) have recently utilized small, relatively simple laboratory microcosms to investigate the biotransformation of selected organic chemicals in several subsurface environments. The microcosms consisted of 35ml or 50ml screw-top test tubes filled with authentic, uncontaminated aquifer material and closed with Teflon-lined screw caps.

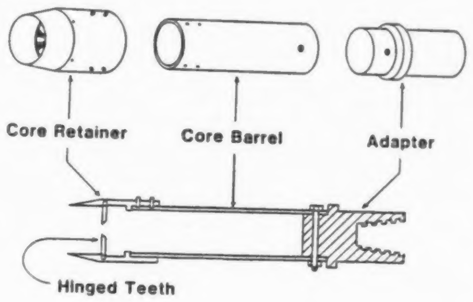

Figure 1. Coring device. (After Wilson et al., 1983)

Aquifer solids were obtained from the subsurface by special coring and extrusion procedures which precluded contamination by surface microorganisms. A bore hole was first drilled to the desired depth with an auger. A barrel equipped with a core retainer (Figure 1) was then placed on the bottom of the hole and pushed into the underlying undisturbed formation. The core thus obtained was extruded by hydraulic ram through a sterile paring device which removed the outer layer of the core that was contaminated by contact with the core barrel (Figure 2). A short length (3-5cm) of material from each end of the core was also removed and discarded because of possible contamination. The core material was extruded directly into sterile glass containers and transported to the laboratory for processing as quickly as possible.

For microcosm preparation, aquifer solids were mixed with a small quantity of sterile ground water to produce a slurry and transferred to sterile 35ml or 50ml screw top test tubes. Sufficient space was left in each tube for 1ml of dose solution consisting of the chemicals to be studied dissolved in filter-sterilized ground water. The tubes were topped off with dose solution to leave no head-space and sealed with Teflon-lined caps. The dose solution was dispersed throughout the

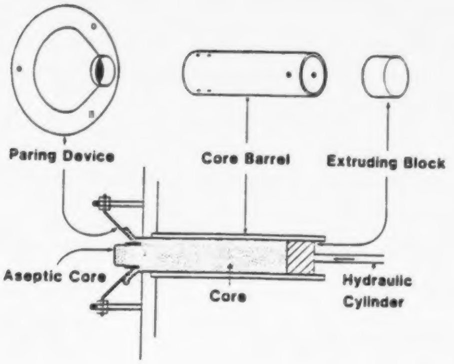

Figure 2. Device to recover cored material aseptically. (After Wilson et al., 1983)

microcosms with a vortex mixer. Abiotic control microcosms were prepared in the same manner, except that the core material was autoclaved (4 hr at 121°C) before dispensing into tubes.

A number of microcosm units were prepared for each experiment, and at least two test units and one control were analyzed initially and at selected intervals (e.g. 1,3, and 9 weeks) after incubation in the dark at appropriate aquifer temperature. Figure 3 shows a microcosm and apparatus employed for sampling. After removal of the cap, the microcosm tube was screwed into a closed 10mm bore Teflon stopcock. A tube containing pure water was then screwed into the other end of the stopcock and the sock was opened. The contents of the tubes were mixed with a vortex mixer, the cock was closed, and the tubes were removed and sealed with Teflon-lined screw caps. After centrifugation to settle solids, the diluted pore water was analyzed by appropriate methods.

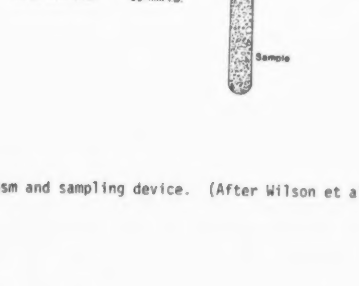

Figure 3. Microcosm and sampling device. (After Wilson et al., 1983)

This methodology has been employed with apparent success for investigating biotransformation processes in several subsurface environments, using various organic pollutants (Wilson, et al., 1983; Wilson, et al., 1984). Except for water movement, it appears to simulate subsurface environments with relative veracity, and probably is reasonably effective in transferring subsurface biotransformation processes to the laboratory where they can be more easily studied. However, there are several concerns and problems which must be recognized in utilizing such methodology.

First, authentic core material, uncontaminated by surface microorganisms, must be acquired from the subsurface environments of interest for microcosm construction. The methodology is thus difficult and expensive, since costly drilling and coring operations using special equipment and techniques are required, as noted above. Studies of subsurface biotransformation processes have been attempted in the laboratory using microcosm systems constructed only with well water (Ehrlich, et al., 1982) or with sterilized sand reinoculated by perfusion with well water (Horvath and Elkin, 1978). However, since there is strong reason to doubt that microbial populations of well water are truly representative of populations occurring in aquifer solids, it is very questionable if these methods are effective in faithfully simulating subsurface environments and, hence, in transferring the biotransformation processes as they occur in the aquifer to the laboratory. Further study of these questions is needed, since elimination of the need for acquiring authentic uncontaminated core materials for microcosm construction would greatly simplify subsurface biotransformation studies.

A second concern in using this methodology is the extent to which the microbial population in a core and, hence, biotransformation processes which will occur in microcosms constructed from this core material, will be representative of the subsurface environment of interest. This is a manifestation of spatial variability problems that plague all investigations of subsurface pollution. Because of the rigid, highly structured nature of the geologic solids matrix comprising the framework of subsurface environments, such environments may exhibit very significant heterogeneity over short distances, both laterally and with depth. Although available information indicates that microbial populations in subsurface regions below the root zone are remarkably uniform in numbers (Wilson and McNabb, 1983), it is highly probable that these populations will often vary significantly in types of organisms, metabolic capabilities, and levels of activity within relatively short distances. For example, microbial populations within lenses of less permeable material within an aquifer are likely to differ in composition and level of activity from populations in the bulk of the aquifer which experience a greater influx of water and, consequently, nutrients and electron acceptors. Similarly, populations within a plume of pollution in an aquifer will likely differ in composition and metabolic capability from populations in the surrounding pristine aquifer material because of adaptation to or inhibition by the pollutants. Hence, if core material for study of biotransformation in an aquifer happened to be obtained from such a lense or plume, the results would not truly reflect the biotransformation processes occurring in the aquifer as a whole.

A third concern and problem with this methodology is related to sensitivity. Because of the difficulty and expense involved in acquiring core material for microcosm construction, these systems are necessarily small, and the volumes of water which can be obtained from them for analysis are limited. Hence, very sensitive analytical methods are required for study of the biotransformation of chemicals at environmentally relevant concentrations using this methodology. Limitations of presently available analytical procedures, however, may cause the methodology to lack sufficient sensitivity to detect and characterize biotransformations occurring at rates that are very slow but that are still likely to be of much importance in subsurface environments because of slow water movement and concomitant long pollutant residence times therein. This was illustrated by Wilson, et al. (1984) in work on the pollution of ground water by polynuclear aromatic compounds at the site of an abandoned wood creosoting plant. Since the site was rather well characterized hydrologically, it was possible to use a mathematical model to estimate the concentrations of naphthalene that would be present in ground water at a boundary 200m from the point of entry over the next 100 years, assuming various rates of biodegradation. These estimates indicated that a degradation rate as low as 5 percent per year would have a substantial effect on the amount of naphthalene reaching the boundary. However, the lowest rate of biotransformation that could be detected using small scale microcosms constructed from core material from the site was approximately 50 percent per year.

Another concern with the methodology is the absence of any means for controlling redox potential in the microcosms. Use of this methodology to date has been primarily for simulating shallow water table aquifers that usually contain low levels of oxygen. In this roll the methodology appears adequate over a period of a few weeks, but over longer periods changes in redox would likely become intolerable.

Finally, an additional potential problem with the methodology is related to the possible contribution to pollutant biotransformation of consortia of microbes living symbiotically in microhabitats within subsurface environments. The slurrying of core material required for microcosm preparation would destroy microhabitats present in the subsurface solids and thus disrupt biotransformation processes mediated by such consortia.

Transport and Fate Study Employing Laboratory Soil Profile Models

Piwoni, et al. (1984), have recently employed methodology involving the use of relatively complex laboratory microcosm systems for investigating processes controlling transport and fate of pollutants in an unsaturated soil profile receiving municipal wastewater amended with selected toxic chemicals.

Microcosms were prepared by packing 10cm increments of soil obtained with great care from a natural sandy soil profile into 15cm diameter borosilicate glass columns. The increments occupied the same relative positions in the columns as they did in the native profile. The soil was neither dried nor screened and was packed into the columns as soon after collection as possible to protect the native biota. The columns were packed to a depth of 150cm, with great care being exercised to achieve uniformity between columns and to attain a hydraulic conductivity essentially the same as that of the native profile.

Figure 4 shows schematically a column and associated components which comprised a complete microcosm system. A closed greenhouse section extended 45cm above the soil surface to provide room for growth of grass and permit recovery of compounds volatizing from the profile. The greenhouse was illuminated with artificial sunlight for 12 hours daily, with the remainder of the column being wrapped in metal foil to prevent light from contacting the soil profile below the surface. A low flow of air, sufficient to replace the air in the greenhouse approximately every eight minutes, was passed continuously through this section. A portion of the exiting air was passed through a trap containing Tenax GC to recover for analysis compounds which volatilized from the soil profile.

Wastewater was mixed with an aqueous solution of test chemicals in a mixing reservoir prior to application to the soil. The solution of test chemicals, prepared aseptically in filter sterilized organic-free water, was stored without headspace in a flexible Teflon bag connected to the mixing reservoir by glass tubing and contained inside a sealed glass flask filled with water. An appropriate quantity of the chemical solution was forced into the mixing reservoir by pumping a measured volume of water into the sealed flask, thus displacing an equal volume of solution from the Teflon bag. The amended wastewater was transferred to the column by siphoning action initiated by applying pressure to the mixing reservoir with nitrogen gas. The mixing and application operations, as well as the lighting sequence for the greenhouse, were microprocessor controlled.

Water in the unsaturated soil profile was sampled by applying a gentle vacuum (30kPa) to sintered glass suction samplers in sampling ports in the wall of the column at depths of 7.5, 15, 30, and 60cm below the soil surface. For analysis of highly volatile compounds, the water sample was collected in a screw top test tube, with a trap containing Tenax GC located on the suction side of the test tube to scavenge volatiles escaping from solution. Both the contents of the tube and trap were analyzed. For analysis of extractable compounds, water from the suction samplers was passed directly through traps containing XAD resin to recover the compounds of interest. Samples of effluent water from the column and influent water from the mixing reservoir were also collected for analysis.

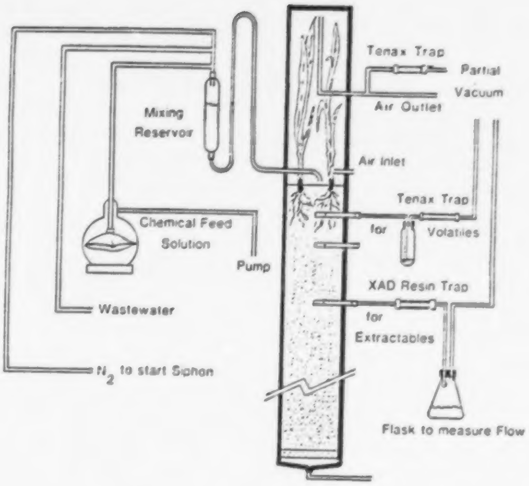

Figure 4. Soil profile microcosm system. (After Piwoni et al., 1984)

In this study, seven microcosm systems were operated. To simulate high rate infiltration land treatment systems, 4.4cm of wastewater was applied to each column daily, with equal portions being applied at 4 hr intervals. Three columns served as controls and received only wastewater for the duration of the experiment (58 weeks). Three columns received unamended wastewater for 18 weeks to allow the soil to acclimate to the wastewater constituents, and then received wastewater amended with selected toxic chemicals for 40 weeks. A seventh column received spring water amended with ammonium nitrate (to support plant growth) for 18 weeks, and then received spring water amended with ammonium nitrate and toxic chemicals for the duration of the study. The purpose of this column was to provide insight regarding the effect of the organic matter and inorganic nutrients of the wastewater on the behavior of toxic chemicals in the soil profile. Since the primary objective of the study was to investigate volatilization and transformation of toxic chemicals, interpretive monitoring was not initiated until 12 weeks after application of water or wastewater amended with toxic chemicals had begun, at which time the sorptive capacity of the columns for the test compounds had been essentially satisfied and steady-state conditions had been attained.

As used by Piwoni, et al. (1984), this methodology appears to have been quite effective for investigation of volatilization and transformation processes occurring in the soil profile. With slight changes in experimental chronology, it could also have been employed for investigation of sorption processes. The methodology is, however, obviously very complex and costly, which is a major problem and concern in its utilization. Extensive fabrication of costly glassware and other components is required in constructing the microcosms. Proper acquisition of appropriate soil profile increments and packing of effective columns is a major undertaking. In particular, preparation of soil columns that are uniformly packed and conform to the parent soil profile in hydraulic and other properties is somewhat of an art, and will usually require the services of an experienced and talented soil scientist. Also, utilization of this methodology will usually involve long periods of operation and the generation of very heavy analytical loads, with concommittant heavy resource and personnel requirements.

Another problem and concern with this methodology pertains to potential inadequacies in preserving the properties of natural soil profiles in the microcosms. The column packing procedure used in the methodology is probably fairly successful in producing in the column a soil profile which is a reasonable fascimile of a natural profile of sandy, non aggregated soil. It would, however, be inapplicable to soil with any appreciable aggregate structure, since such structure would be destroyed in the packing process. A method which captures undisturbed natural soil profiles for use in laboratory studies of subsurface processes would be much preferred.

Difficulties in distinguishing between transformation processes are also inherent to this methodology because of problems encountered in eliminating all biological activity in the columns without altering other soil properties and the cost and effort required to set up sterile control microcosms. In addition, there are problems in detecting and characterizing processes that occur at slow rates, but that may be important in subsurface environments. If the rate of water application to the column is decreased to increase pollutant residence time in the soil, the opportunity for detecting slow processes will be increased but the length of the experiment is likely to become prohibitive. Similarly, if column length is increased in an effort to detect and characterize slow processes, operational problems and costs are likely to become unacceptable.

Field Study of Pollutant Transport and Fate in the Saturated Zone

During recent years, considerable research has been conducted at Stanford University pertaining to the effects on ground water quality of recharging an aquifer by direct injection of reclaimed municipal wastewater. Roberts, et al. (1982), have reported on aspects of this work which involved field (in-situ) investigation of processes governing the transport and fate of organic pollutants in saturated subsurface environments.

This research was conducted in an aquifer composed of a layer of relatively homogeneous silty sand ranging in thickness from 1.5 to 3m and located at a depth of 10-15m below the surface of the ground. The formation was underlain by an impermeable clay layer and overlain by relatively impermeable, interbedded layers of clay and silty sand. Tertiary wastewater was injected directly into the aquifer through a recharge well, and the effects on ground water were monitored at several strategically located observation wells. An aquifer section indicating the relative locations of the recharge and observation wells is shown schematically in Figure 5.

Observation wells were drilled by means of a hollow stem auger to avoid the use of drilling fluid which might contaminate the aquifer and interfere with subsequent ground-water sampling. The wells were cased with 2cm diameter threaded polyethylene tubing connected without adhesives which might also cause contamination problems. In most wells, the casing was slotted through the full length of the permeable zone. Pressure in the aquifer during recharge was sufficient to ensure artesian flow of the monitoring wells. This precluded the need for pumping to obtain samples of ground water and greatly simplified the sampling procedure.

The native ground water in the aquifer was more than tenfold higher in chloride content than the injected wastewater. Therefore, movement of injected water through the aquifer was traced by decreases in chloride concentrations of ground water at the observation wells. Ground water samples from the observation wells were analyzed periodically during the recharge operation for several halogenated organic compounds present at low concentrations in the injected water to establish breakthrough curves for these compounds. Retardation of movement of the compounds due to sorption on the aquifer solids was determined by comparison of their breakthrough curves at specific observation wells with analogous breakthrough curves for injected water.

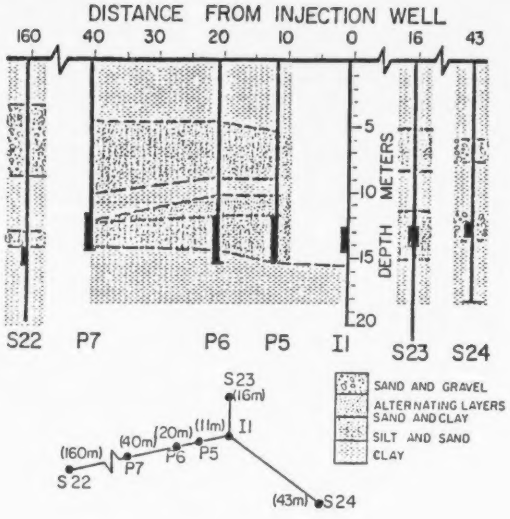

Figure 5. Aquifer section showing relative locations of wells at recharge site. (After Roberts et al., 1982)

There was no evidence for transformation within the aquifer of any of the monitored compounds during the period of wastewater injection. At those observation wells where complete breakthrough occurred, these compounds were present in concentrations essentially the same as in the injected water. However, there was reason to question if the residence times of the monitored compounds in the aquifer between the injection and observation wells were sufficiently long to permit detection of slowly occurring transformations. Therefore, selected halogenated organic compounds were monitored for one year after cessation of wastewater injection at an observation well in a portion of the aquifer which had been saturated in regard to sorptive capacity for these compounds during the injection operation. Significant decreses in concentrations of the monitored compounds during this time were concluded to be the result of transformation processes. The only other plausible explanation for the observed concentration decreases, dilution, was precluded because ground water flow in the region was shown by isotope tracer studies to be extremely slow, and because the rates of decrease for different compounds, which should have been very similar had they resulted only from dilution, were also different.

This field (in-situ) investigation was relatively effective in detecting and providing insight regarding sorption and transformation processes affecting pollutant transport and fate in the subsurface. There were several major and relatively unique factors which contributed to this success. These included: the unusual degree of experimental control afforded by the confined, well defined, relatively homogenous aquifer in which the study was conducted; the natural tracer system for water movement provided by the large difference in chloride content of the injected water and native aquifer water; and, simplified sampling of the observation wells permitted by the artesian flow of water from the aquifer. Such a fortuitous set of circumstances is not often encountered in field studies. Nevertheless, if this investigation is examined objectively, a number of problems and concerns pertaining to field (in-situ) methodologies for subsurface processes research can be discerned.

First, such methodologies require the sampling of subsurface waters at a sufficient number of locations within the area of study to clearly define water and pollutant movement and to detect meaningful concentration changes. This usually requires installation of a number of costly sampling wells capable of providing representative, uncontaminated ground water samples. Special drilling techniques that do not contaminate the aquifer must be used, and materials for well casing and completion must be consistent with the objectives of the study, neither adding any interfering substances to samples through leaching nor removing any constituents through sorption or other mechanisms. Also, pumps and other equipment used for obtaining samples of ground water from the wells must be both non-contaminating and non-sorbing.

A second problem in field methodologies pertains to difficulties in determining locations for sampling points, both in the horizontal plane and in depth, due to frequent heterogeneity of subsurface environments across relatively short distances. Thus, if a sampling well is drilled in a location or screened at a depth which is wrong by only a very few meters, a plume of polluted ground water may be missed entirely. Unlike an analogous situation in air or surface water studies, this will be a very costly mistake, since drilling and completion of an additional expensive well will be required to achieve the necessary change in location of the sampling point.

Another problem is the need to employ tracer substances in field studies to accurately determine water movement in the subsurface. Such substances must behave essentially the same as water molecules in subsurface environments, being neither retarded in movement by sorption on subsurface solids nor attenuated in concentration by transformation processes. Unfortunately, substances which can serve effectively as tracers often cannot be introduced into the subsurface for experimental purposes because of possible deleterious effects on ground water quality, and seldom are present naturally at appropriate concentrations in subsurface waters, as was the case in the study described above.

Difficulty in distinguishing between processes responsible for changes in pollutant concentrations is yet another concern in field methodologies for subsurface process studies. In the study described above, decreases in concentrations of selected halogenated hydrocarbons which occurred over a prolonged period of observation and could not be attributed to other processes provided strong evidence for transformation of these substances in the aquifer. However, there was no basis for determining if these transformations resulted from biological processes, or if abiotic processes were partly or wholly responsible. Obviously, establishing a sterile control system in a field situation is usually a very remote possibility. Similarly, it is often difficult to determine if the failure of a pollutant to appear in significant concentrations at an observation well over a prolonged period of observation is due to transformation of the compound in the aquifer between the source and observation well, or is the result of sorption or dispersion processes.

Additional readily apparent problems and concerns with field methodologies for subsurface process research pertain to needs for detection and charcterization of processes occurring at very slow rates and for replication and repetition of experiments. Field investigation of processes that occur at very slow rates in subsurface environments, but that may be important because of long pollutant residence times therein, requires monitoring of pollutant concentrations over long periods of time and/or over long distances of pollutant travel. This is likely to be excessively expensive because of the need for prolonged field and supporting laboratory operations and installation of many costly observation wells. Also, there is usually little opportunity in field studies to replicate or repeat experiments. Because of physical limitations, it is usually almost impossible to establish two or more identical experimental systems for investigation of subsurface processes in field situations. Also, by the time an initial experiment has been completed in a field study of subsurface processes, the experimental system is likely to have undergone sufficient change, primarily as a result of exposure to pollutants, to preclude exact repetition of the experiment.

CONCLUSIONS

The investigations outlined above demonstrate a few of the methodological concepts employed in research pertaining to the processes governing transport and fate of pollutants in the terrestrial subsurface, and are indicative of many of the major methodological problems encountered in such research. These investigations clearly show that both laboratory and field (in-situ) methodologies are useful in subsurface processes research. It is obvious that laboratory methodologies possess advantages over field methodologies in regard to cost, labor requirements, control of variables, and opportunity for replication and repetition of experiments. However, there are numerous uncertainties concerning the effectiveness of laboratory methodologies in transferring subsurface processes from the field to the laboratory and, hence, the extent to which process information gained by use of such methodologies is truly reflective of in-situ processes. Subsurface processes research is likely to be most effective if both laboratory and field methodologies can be employed simultaneously and in a complimentary manner, with laboratory studies being used to guide and confirm field work.

The studies described above also clearly reiterate that research pertaining to subsurface transport and fate processes, whether conducted in the laboratory or the field, will almost invariably involve formidable methodological problems. Thus, such research will likely be very laborious and expensive, particularly in comparison to analogous research in other environmental media.

The major problems in investigative methodology for subsurface processes research appear to result primarily from three principal characteristics of the terrestrial subsurface. The first, and perhaps dominant, of these characteristics is remoteness and difficult accessibility. The acquisition of authentic, uncontaminated samples of water and/or solids from remote and relatively inaccessible subsurface environments is required for both laboratory and field investigations of subsurface transport and fate processes, either for construction of laboratory microcosms or for field monitoring activities. This entails special problems in drilling and completion of sampling wells, coring operations, and sampling apparatus and techniques.

A second characteristic of the subsurface contributing significantly to methodological problems in subsurface processes research is the highly structured nature and attendant heterogeneity across relatively short distances of subsurface environments. This characteristic is a principal cause for difficulties in preserving the properties of parent subsurface environments in laboratory microcosm systems, and is responsible for problems in determining the proper locations for obtaining cores of subsurface solids to ensure that laboratory microcosms constructed from these materials will be representative of the subsurface compartments of interest. It is also the cause for difficulties in determining the proper location for sampling points which will permit effective observation of subsurface transport and fate of pollutants in field investigations.

Finally, the characteristically slow rate of movement of water and pollutants in subsurface environments, which usually results in long residence times for pollutants within these environments, necessitates that methodologies for subsurface processes research possess the capability for detecting and characterizing processes which occur at very slow rates. Hence, this characteristic is largely responsible for methodological problems pertaining to sensitivity and long term operation of experimental systems in both laboratory and field studies.

Obviously, there is need for much improvement in investigative methodologies for research pertaining to the processes that govern transport and fate of pollutants in subsurface environments. Advances in a number of diverse areas, including particularly geophysical methods, chemical analysis procedures, microcosm technology, and drilling, coring, and well completion techniques, will be required to accomplish this improvement.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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DIELECTRIC PROPERTIES OF SATURATED SOILS

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ABSTRACT

Characterizing the flow of two fluid components in a porous structure is a complex task. There is a need for new investigative techniques which will determine the time evolution of the flow. This research is directed to developing a time resolved measuring method based on microwave techniques. The porous material is interrogated by a microwave impulse and its response is used to determine the dielectric properties of the composite structure consisting of the soil and saturating fluids. The dielectric constant of the composite material can be related to the saturating fluid content.

The object of this investigation is to determine the feasibility of using the dielectric constant of saturated soils to characterize their fluid content. The large difference in the dielectric constant of water and soil components indicates the composite dielectric constant of the wet soil is strongly dependent on the water content. The initial stages of this investigation focused on three areas. First, a measurement technique to obtain the dielectric constant of saturated soils was established. Second, the relationship between the measured dielectric constant and the volume of saturating fluid was determined. Finally, a variety of fluid saturants were used in the measurements which emphasized the behavior of immiscible organic fluids, particularly those which are not susceptible to any appreciable biological degradation on a long term basis.

INTRODUCTION

A microwave measuring technique is applied to monitoring the behavior of water in coarse sand. Because of the large dielectric constant of water compared to other fluids, the presence of water dominates the electromagnetic behavior of soils. Dynamic flow characteristics of a combination of water and an immiscible fluid are determined from the time dependence of the dielectric constant of the saturated soil.

The measuring method was chosen to minimize ambiguity in defining the dielectric constant of composite materials. A method was developed which determines the velocity of propagation of an electromagnetic impulse in the saturated soil. The velocity of this impulse C is related to the composite dielectric constant of the saturated soil (ε_C) by

$$C = C_0/\sqrt{\varepsilon_C} \qquad (1)$$

where C_0 is a constant $C_0 = 3 \times 10$ m/s. The composite dielectric constant is then calculated from

$$\varepsilon_C = [C_0/C]^2 \qquad (2)$$

this relationship yields an unambiguous means of determining the composite dielectric constant (ϵ_C) of the saturated soil. Although this technique offers advantages in interpreting the results, there are demanding requirements on the measurement of time. The time resolution is less than a nanosecond (10^{-9}sec) and requires rather sophisticated sampling techniques.

The saturated soil sample is contained in a coaxial waveguide. The electromagnetic modes of the coaxial waveguide include a zero order dispersionless mode. This mode affords a simple propagating wave, the velocity of which is dependent on the dielectric constant of the material filling the waveguide (the saturated soil) and not on any frequency or geometric influences of the waveguide itself.

The frequency spectrum of the electromagnetic impulse is in the microwave range. A short impulse is necessary to obtain the time resolution of the measurement and thus, microwave frequencies are used. A second factor dictating microwave frequencies is that the dispersion due to dissolved ions is less at the higher microwave frequencies thus simplifying the interpretation of the measurement.

This measuring technique was applied to a loose sand saturated with a variety of organic fluids and water. The porosity and geometry of the loose sand were held constant, while the composite dielectric constant was measured for various saturation fluids. The dielectric constant of the saturating fluids varied from one (air), to 78 (water), which in turn, altered the composite dielectric constant: A plot of the composite dielectric constant as a function of the dielectric constant of the saturating fluid is shown in Fig. 1. A variety of immiscible organic fluids was used in this measurement including carbontetrachloride, trichloroethylene, and dichlorethane. A model for predicting the composite dielectric constant based on a knowledge of the porosity of the soil and the dielectric constants of the components can be constructed. This model is called a volume fraction model and is given by

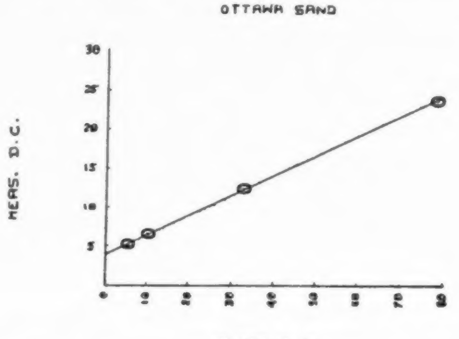

Figure 1. The measured, composite dielectric constant (D.C.) as a function of the fluid dielectric constant of a saturated coarse sand. The curve is computed from Eq. (3).

$$\varepsilon_0 = \varepsilon_S(1 + \phi) + \varepsilon_F\phi \qquad (3)$$

where ϕ is the porosity, ϵ_C is the measured composite dielectric constant, ϵ_S is the dielectric constant of the soil and ϵ_F the dielectric constant of the fluid. This equation is shown as a solid line in Fig. 1 and agrees well with the measured values. This equation can then be used in the inverse manner to determine the fluid saturation. If the composite dielectric constant is measured and the saturating fluid and soil type are known, the water volume can then be calculated. This relationship is accurate for all the fluids considered except water. The largest deviation occurs with water. It is believed that the water interacts more vigorously with the soil than do the other fluids. Inhibition of the rotation of the rather large permanent dipole moment of the water molecule leads to a reduced dielectric constant. The behavior of water in soils is influenced by complex interactions which are affected by the presence of other fluids. This combination of affects which are present with water is the subject of the proposed research. The microwave dielectric measurements have been demonstrated to differentiate between types of fluiid behavior in the soil using the volume fraction model discussed above. Using this model as a means of establishing the simplest fluid/soil behavior, it will be possible to determine affects due to water/fluid/soil interactions.

The microwave measuring technique determines ϵ_C in an almost continuous manner so that time variations of the system parameters can be observed. The dynamic flow apparatus consists of a coaxial waveguide filled with soil. Flow of the fluid is controlled by a set of valves external to the waveguide. The flow rates are at relatively low velocities to simplify the hydraulic behavior. The percentage volume of water (wetness) is then determined as a function of time as the flow components are changed. The rate at which the immiscible fluid replaces the bulk water is then measured for a particular soil. Particular cases of interest are immiscible fluids which are resistant to biological degradation such as carbontetrachloride. The time sequence of the combination of carbontetrachloride and water are meant to immitate a spill of organic fluid on either wet or dry coarse sand and the subsequent flooding with water.

The first sequence of fluids involves the saturation of the sand by carbontetrachloride and the subsequent flushing with water. The volume of carbontetrachloride which remains in the sand is also determined as a function of time by an independent measurement. The time sequence of the dielectric constant is shown in Figure 2 where the initial state is complete saturation with $C\,Cl_4$. The composite dielectric constant increases rapidly as water replaces the $C\,Cl_4$. At later times the dielectric constant becomes constant. The increase in dielectric constant occurs because water's dielectric constant is so much larger ($\epsilon_W = 78$) than carbontetrachloride ($\epsilon_F = 2.62$). The time dependence of the volume of water substituting for the $C\,Cl_4$ follows a similar curve (Fig. 3). The volume measurements indicate that less than 1% of the original $C\,Cl_4$ volume with most of the fluid in the flushed sand being water. If we compare the value of the dielectric constant measured after flushing, with that for a sand filled initially with water, (no $C\,Cl_4$ introduced), we notice a difference. The dielectric constant for the $C\,Cl_4$ coated sand is less than that of the clean sand with full water saturation. This may result from the interaction of the water with the $C\,Cl_4$ coated surface being different than that with a clean quartz surface.

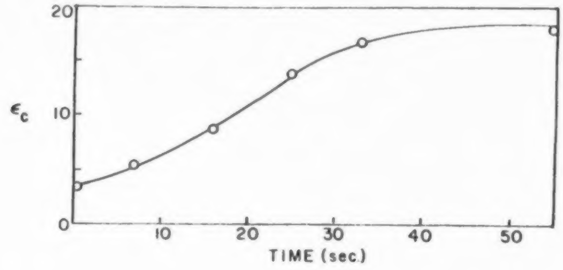

Figure 2. The measured composite dielectric constant (ϵ_C) as the system is being flushed with water. The initial saturant of the coarse sand is carbontetrachloride.

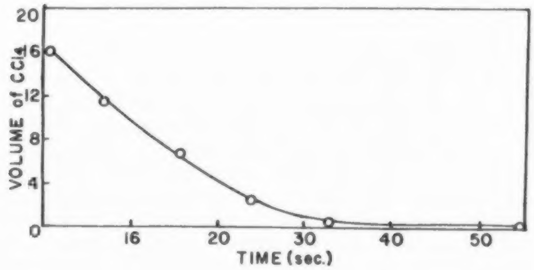

Figure 3. The volume of carbontetrachloride remaining in the coarse sand as it is flushed with water.

A second fluid sequence involves flooding an initially water saturated sand (compared to a dry sand in the first sequence) with first $C\,Cl_4$ and then with water. The decrease in dielectric constant after flooding with $C\,Cl_4$ (Fig. 4) results from the removal of the water from the sand. The resultant dielectric constant after a reasonable period of time indicates that a small percentage (25%) of the water still remains in the sand. The measured composite dielectric constant is smaller than that predicted by Eq. (1) based on the known volumes. The lower measured composite dielectric constant indicates inhibited dipolar motion for the remaining water.

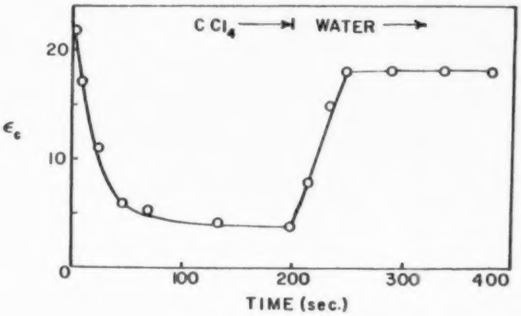

Figure 4. The composite dielectric constant as the system is flushed first with carbontetrachloride then with water. The coarse sand is initially saturated with water.

When the waveguide is flushed with water, the composite dielectric constant again rises. As in the previous experiment almost (>99%) all the carbontetrachloride is eventually replaced by water. The composite dielectric constant reaches a maximum value which is again below the initial water saturated value. This is attributed to the interaction of the carbontetrachloride coated sand grains and water molecule motion. The dielectric constant is not the only property altered by flushing with $C\,Cl_4$. The hydraulic conductivity of water moving thorugh the coated grains is observed to be reduced approximately 40% compared to that in uncoated sand. Both these effects demonstrate the motion of the water molecules is inhibited by the presence of an immiscible fluid and the effect of the interaction is considerably larger than single molecular dimensions. This interaction is important in defining the transport and storage properties of water in the presence of an immiscible fluid.

ACKNOWLEDGEMENTS

This work was supported by the Department of the Interior, Environmental Protection Agency, and the National Science Foundation (CEE-8019278).

THE COMBINED USE OF GENOTOXICITY AND WHOLE EMBRYO TERATOGENICITY SCREENING ASSAYS IN PREDICTING TERATOGENIC RISKS

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ABSTRACT

Whole amphibian embryo teratogenicity assays are useful for predicting risk to aquatic species. However, extrapolation of data to other systems is difficult because of differing metabolisms and other factors. One way to make whole embryo teratogenicity assays more predictive is to understand which molecular mechanisms are inhibited. If such mechanisms are common to many species, then results of both assays complement one another. Our whole embryo teratogenicity assay uses embryos of the frog *Xenopus laevis*. Endpoints measured were 96 h lethality, malformation, growth, and the teratogenicity index (LC50/EC50 malformation). Our genotoxicity bioassay measures the ability of a substance to alter RNA or protein biosynthesis. This assay involves treatment of the plasmid pHSV-106 containing the herpes thymidine kinase (TK) gene with the test substance. The plasmid is then microinjected into *Xenopus* oocytes and the amount of TK made is assayed. The second genotoxicity assay involves injecting TK gene, exposing the oocyte, and then measuring TK production. This assay measures the agent's ability to interfere with the metabolic machinery that makes protein. We have validated both assays using known inhibitors of DNA, RNA and protein synthesis.

INTRODUCTION

Because of the thousands of chemicals already released into the aquatic environment and many other new chemicals that will soon be released, short-term tests have been developed to screen for mutagens, carcinogens and teratogens. Mutagenicity and carcinogenicity tests have already been developed and are now in use as screening assays (Ames, et al., 1973; Evans, 1976). However, there are no established teratogenicity screening assays capable of predicting hazards to both aquatic organisms and human health. Our goal is to develop a teratogenicity screening assay that is not only rapid but also has wide predictive utility. This short-term test is based on the knowledge that many genotoxins are also teratogens and that normal gene expression plays a critical role in the development of all organisms. Our assay includes a whole embryo bioassay using the embryos of the South African clawed frog, *Xenopus laevis*, and a genotoxicity and gene expression assay that measures the ability of a xenobiotic substance to interfere with the structure or expression of the herpes thymidine kinase (TK) gene microinjected into *Xenopus* stage 6 oocytes.

MATERIALS AND METHODS

Whole Embryo Assay

Animal Care and Breeding

Adult *Xenopus* were obtained from *Xenopus* I® , Ann Arbor, Mich. and stored in glass aquaria for a minimum of 30 days until use. Adults were fed beef liver and lung obtained from a local packing house. Twelve h prior to mating, the female was injected with 1000 I.U. of human chorionic gonadotropin (Sigma® , St. Louis, Mo.) and the male received 400 I.U. into the dorsal lymph sac. Amplexus ensued within 4-6 h and egg deposition 9-12 h from the time of injection.

After breeding, the adults and any fecal material were removed from the tank and the embryos obtained by scraping the eggs into 55 mm plastic Petri dishes. The jelly coats of the embryos were removed by swirling for 2-3 min in a 2% w/v cysteine solution (pH 8.1).

Normally developing blastulae were initially selected by first removing them from necrotic eggs and abnormally cleaving embryos. A second selection was then performed to ensure that only normal embryos were used in the test. For each toxicant concentration, there were two groups of embryos of twenty each placed into 55 mm glass Petri dishes.

Test Substances and Data Collection

Test substances were dissolved in aerated tap water in different concentrations. Solutions were changed once every 24 h after each set of observations were recorded. Great care was taken to prevent damage to the embryos during the change. At 24, 48 and 72 h the dead embryos were scored and removed from the dishes. The number malformed and the stage of development according to Dumont, et al., (1983) were recorded. Death at 24 and 48 h had to be ascertained by the embryo's skin pigmentation, structural integrity and irritability while at 72 and 96 h, the lack of heartbeat in the transparent embryo was an unambiguous sign of death. At 96 h, the number of dead and malformed embryos was recorded for each group. Surviving embryos were fixed in 0.5% formalin and the head-tail length of each embryo was measured using a Radio Shack® digitizer and the data input directly to a Radio Shack® model 16 microcomputer. Mortality and malformation endpoints were analyzed by the Litchfield and Wilcoxon test (1949) and growth was analyzed by Student's tTest for grouped observations.

The Genotoxicity and Gene Expression Assay

The ability of a compound to inhibit macromolecular synthesis directly through DNA damage or indirectly by affecting the processes of transcription or translation was investigated by the use of two assays: the Gene Exposure Assay and the Oocyte Exposure Assay. In both tests, the plasmid pHSV-106 (Bethesda Research Laboratories®) which contains the TK gene was micro-injected into *Xenopus* stage 6 oocytes using the procedure of Kressman and Birnstiel (1980).

For the Gene Exposure Assay, the pHSV-106 DNA was exposed *in vitro* to various concentrations of known inhibitors of macromolecular synthesis for 2 h prior to injection. After this time, the DNA was separated from the inhibitor using gel filtration chromatography, concentrated by lyophilization and injected into the germinal vesicles of oocytes. After injection, the oocytes were incubated at 23°C for 20 h and the processed for TK activity (Brinster, et al., 1981). Any destruction of the DNA by a genotoxic substance would result in less TK activity observed.

For the Oocyte Exposure Assay, pHSV-106 was injected directly into the germinal vesicle. Then the oocytes were exposed to different concentrations for known inhibitors of DNA, RNA and protein synthesis for 20 hr. After this time, the oocytes were processed for TK activity. Inhibitors that interfered with gene expression at any level would reduce the amount TK activity.

RESULTS AND DISCUSSION

The Whole Embryo Bioassay

Dumont, et al., (1983) have described the Frog Embryo Teratogenesis Assay, *Xenopus* (FETAX) used in this study. We have used a variety of inhibitors of DNA, RNA and protein synthesis to further validate this system. Figure 1 shows a normal (top) 96 h larva and a larva that has been treated with the DNA synthesis inhibitor cytosine arabinoside (bottom). The embryos are transparent thereby facilitating the scoring of dead and malformed embryos. The heart is easily visible at 96 h so the estimation of death is unambiguous. The malformed embryo shows that it is also easy to score malformations. Reduced cranial and optic structures, abnormal pigmentation, tissue edema, abnormal digestive tract and deformed tail are malformations frequently seen. We are able to use 40 embryos at each concentration which aids in the establishment of narrow confidence ranges for the 96 hr EC50 malformation and the LC50.

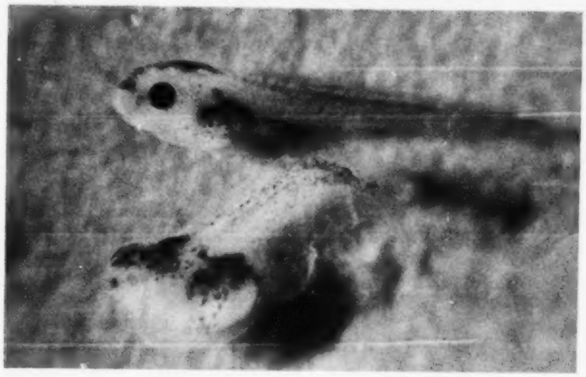

Figure 1. Normal 96 h Xenopus larva (top) and larva exposed to the DNA synthesis inhibitor cytosine arabinoside (bottom).

Our validation study showed that DNA synthesis inhibitors such as hydroxyurea, cytosine arabinoside and ethidium bromide were teratogenic while the RNA synthesis inhibitor actinomycin D and the protein synthesis inhibitor cycloheximide were toxic but not teratogenic. Naphthalene, a polycyclic aromatic hydrocarbon, proved to be acutely toxic but not teratogenic. DNA synthesis inhibitors have been shown to be teratogenic in mammalian systems while RNA and protein synthesis inhibitors generally affect only growth (Ritter, 1977). Figure 2a shows the dose-response curve for 96 h of hydroxyurea treatment. The malformation curve is clearly separate from the mortality curve. The 96 h LC50 is 1.82 mg/ml and the 95% confidence interval is 1.5-2.7. The great number of embryos used allows narrow confidence limits to be set. The teratogenicity index (LC50/EC50) is 4.3. A value greater than 1.5 indicates significant teratogenic risk as the test substances deforms the embryo without causing death. Figure 2b shows that naphthalene is not teratogenic because the two curves are almost superimposed on one another. The teratogenicity index for naphthalene is 1.13.

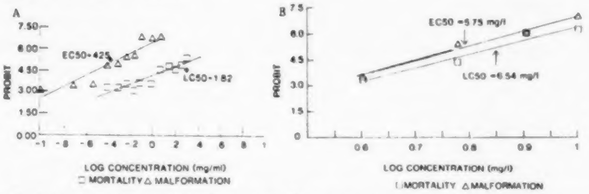

Figure 2. The Effects of Hydroxyurea and Naphthalene on Xenopus Mortality and Malformation. (A.) Hydroxyurea, (B.) Naphthalene. Naphthalene test was static but in a closed system.

We tested the ability of the whole embryo bioassay to detect actual environmental teratogens present in surface water. Several water samples were obtained from the Tar Creek area of Oklahoma where the water has high concentrations of lead and zinc. One sample (not shown) taken from above the Tar Creek area was neither toxic nor teratogenic while the other two samples showed the presence of aquatic borne teratogens. Undiluted farm pond water caused death in all embryos but dilutions of this water proved far more teratogenic than toxic (Figure 3). The Tar Creek and highway 10 sample was extremely teratogenic as none of the embryos died but all were malformed in undiluted water. This data shows the need to screen for environmental teratogens.

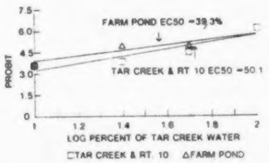

Figure 3. The Effects of Tar Creek Water on Xenopus Mortality and Malformation.

The Genotoxicity Assay

We used the same genotoxic compounds to validate the genotoxicity assay as the whole embryo assay plus the DNA and RNA synthesis inhibitor daunomycin. Actinomycin D and daunomycin bind to DNA and prevents its use as a code for protein synthesis. As expected, these substances stopped TK expression in the Gene Exposure Assay. Figure 4a shows that actinomycin D pretreatment completely inhibits TK expression in *Xenopus* oocytes compared to the control. Actinomycin D and cycloheximide (Figure 4b) both inhibited TK expression in the Oocyte Exposure Assay as expected but cycloheximide has no effect in the Gene Exposure Assay as it inhibits at the level of the ribosome. All substances tested behaved according to their known mode of action except for daunomycin in the Oocyte Exposure Assay.

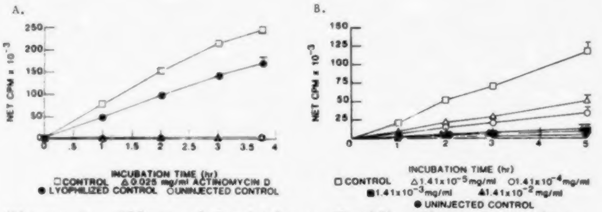

Figure 4. Effect of Genotoxins on Thymidine Kinase Expression. (A). Effect of Actinomycin D in the Gene Expression Assay. (B). Effect of Cycloheximide in the Oocyte Expression Assay.

By combining data from both assays, we have observed that the inhibition of macromolecular synthesis results first in growth inhibition and then slows the rate of development. DNA synthesis inhibitors are highly teratogenic but RNA and protein synthesis inhibitors do significant damage by slowing development and reducing embryo size. The types of inhibitors used in this study seem to give the same results regardless of the species tested. Any other substance that inhibits in a similar manner will most likely cause the same type of defects.

ACKNOWLEDGEMENT

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STATISTICAL EXAMINATION OF SMALL-SCALE SPATIAL VARIABILITY OF VOLATILE ORGANIC COMPOUNDS AND INORGANIC ANIONS IN GROUNDWATER

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ABSTRACT

One approach to the study of processes governing the fate of chemical contaminants in groundwater is the detailed examination of previously contaminated systems. A chi-square analysis of the distributions of nine volatile organic compounds (VOCs) and three inorganic anions in the groundwater in unconsolidated sediments beneath an abandoned landfill near Ottawa, Ontario indicates that the small-scale (1 m) spatial variability of contaminant concentrations is significantly higher for VOCs than for inorganic species. While concentration-versus-depth profiles for inorganics are relatively "smooth", corresponding VOC profiles are highly irregular, with concentrations in points spaced one meter apart often differing by one to four orders of magnitude. Differences in spatial heterogeneity between three VOCs and the inorganic species were statistically significant close to the inferred source area, but non-significant in wells further down-gradient. The description of the spatial distribution of contaminants in unconsolidated aquifers may therefore require a much higher density of sampling points for VOCs than for inorganic species.

INTRODUCTION

In any investigation of the physical and chemical behaviour of contaminants in hydrogeologic systems, the spatial distribution of those contaminants must be accurately determined. Designing monitoring networks which incorporate a sufficiently high density of sampling points requires an appreciation of the spatial variability of the chemical species of interest.

Several studies of groundwater systems contaminated by landfill leachate have indicated that inorganic species tend to adopt relatively "smooth" distributions (e.g., Nicholson et al., 1983; Baedecker and Back, 1979). In this study, we have investigated the degree to which the spatial distributions of volatile organic compounds (VOCs) mimic the smooth distributions observed for inorganic species within such a system. A high density of sampling points at the field site has enabled us to examine the spatial variability of both organic and inorganic species concentrations on a scale of 1 m.

The geology and groundwater flow regime at the Gloucester site have been described by Bahr (1983). An aerial map is provided in Figure 1. The landfill is situated atop a series of glacial outwash deposits composed largely of sand and gravel, with two principal zones of high conductivity separated by discontinuous layers of stratified silt and clay. Groundwater flow is predominantly horizontal within the more conductive zones, and the water table lies at a depth of 5m or less throughout the site.

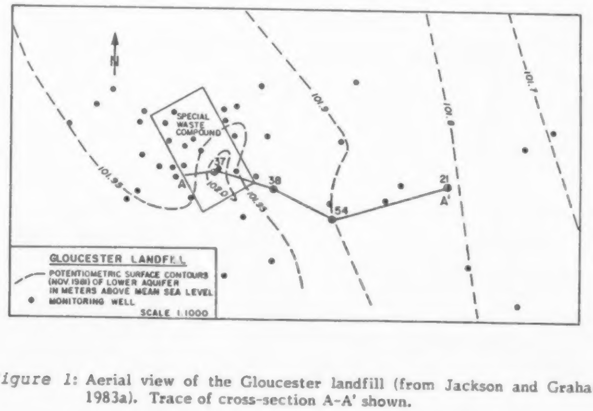

Figure 1: Aerial view of the Gloucester landfill (from Jackson and Graham, 1983a). Trace of cross-section A-A' shown.

The disposal of domestic refuse at the site commenced in the late 1950's and ended in the middle of the 1970's. Hazardous waste liquids were first brought to the site in 1957. Initially distributed throughout the original landfill area, the disposal of organic solvents and pesticides was confined to a fenced area known as the "Special Waste Compound" (SWC) near the end of the 1960's and discontinued in 1978 (Lockwood and Priddle, 1983).

METHODS AND MATERIALS

Groundwater samples were taken from multilevel bundle piezometers (Cherry et al., 1983), consisting of up to nineteen polyethylene tubes surrounding a center stock of polyvinyl chloride (PVC), with adjacent sampling points spaced at 1m depth intervals. Miller (1982) has shown that PVC is neither a source nor a sink for significant quantities of halogenated VOCs. To test the suitability of polyethylene in this regard, VOC concentrations in samples obtained from polyethylene and polytetrafluoroethylen (Teflon®) tubes accessing the same point in a monitoring well in the SWC were compared using an analysis of variance. No systematic differences could be discerned between VOC recoveries using the two matrials (Barbash, 1983).

All of the samples analyzed for VOCs were taken using a newly-designed Volatile Organics Sampler (VOS), originally described by Barbash (1983), and later modified by Lockwood and Priddle (1983). Used in conjunction with a peristaltic pump, this device obtains samples upstream from the pump, thereby avoiding contact between the water and the silicone tubing which these pumps employ. VOC concentrations were determined by the "purge-and-trap" technique (Bellar and Lichtenberg, 1974). Concentrations of inorganic anions in groundwater samples were measured by ion chromatography.

STATISTICAL ANALYSIS

Figure 2, Figure 3 and Figure 4 compare the distribution of chloride along the cross-section A-A' with those of sulfate, trans-1,2-dichloroethylene and toluene, respectively. The data are plotted on a logarithmic (base 10) scale in order to accomodate the

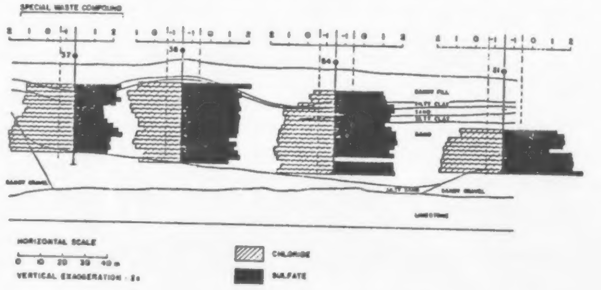

Figure 2: Concentrations of chloride and sulfate (in mg/l) along A-A'

broad concentration ranges observed. Where a given species was not detected, its concentration was assigned to be its limit of detection (indicated by a dotted line on each histogram).

To examine differences in spatial variability on a quantitative basis, we introduce the parameter LOG(R)—the absolute value of the logarithm of the ratio (R) between the concentrations of the species in question at two vertically adjacent sampling points. Thus, the absolute differences between adjacent bar lengths in Figures 2, 3 and 4 are directly proportional to the ratio R for each pair. The spatial variability of a selected species may therefore be expressed as a frequency distribution of LOG(R) values, using all pairs of adjacent sampling points. Since the concentrations of VOCs measured at the Gloucester site span nearly five orders of magnitude, LOG(R) values for all of the chemical species were arbitrarily subdivided into groups separated by integral orders of magnitude, i.e., $0 \leq LOG(R) < 1.0$; $1.0 \leq LOG(R) < 2.0$; $2.0 \leq LOG(R) < 3.0$; and $3.0 \leq LOG(R)$. Figure 5 is a compilation of histograms which display the distribution of LOG(R) values among these four size ranges, for three inorganic and nine organic species detected in four multilevel wells at the Gloucester site.

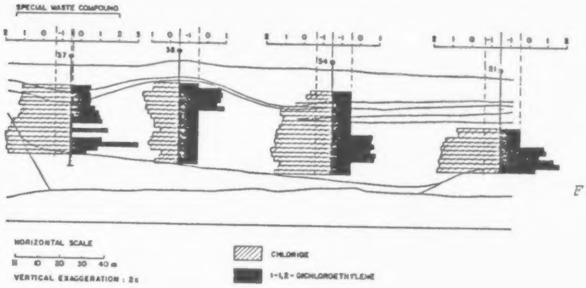

Figure 3: Concentrations of chloride (mg/l) and t-1,2-dichloroethylene (ug/l) along A-A'

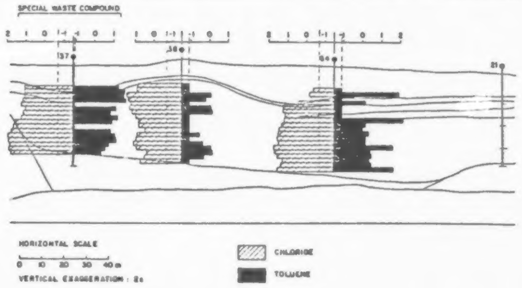

Figure 4: Concentrations of chloride (mg/l) and toluene (ug/l) along A-A'

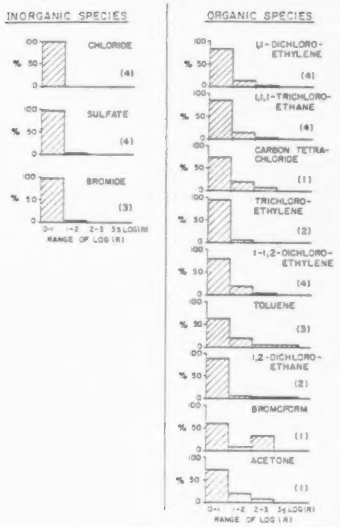

Figure 5: Distribution of LOG(R) among four range classes for inorganic and organic species. Number of wells used for each species included in parentheses.

In order to determine whether differences in LOG(R) distributions —and hence differences in spatial variability—among different species or groups of species were statistically significant, the chi-square test was employed (Zar, 1974), using a conservative, pre-selected Type-I error rate of 0.01. (It should be noted that this use of the chi-square test may have been adversely affected by the possible non-independence among adjacent LOG(R) values.) All exact probabilities were obtained using the interactive statistical computer package SPEAKEZ (Speakeasy Corporation; Chicago, Illinois).

To maximize the number of comparisons, only those chemical species which were detected in all four of the wells sampled (chloride, sulfate, 1,1-dichloroethylene, 1,1,1-trichloroethane and trans-1,2-dichloroethylene) were examined. Since chloride is most commonly measured as a routine chemical parameter in groundwater studies, it was selected as a reference against which the remaining four species were compared. The results from these comparisons (see Table 1) show that, while no difference in spatial variability was observed between the two inorganic species ($P = 1.0$), significant differences were observed between chloride and the three VOCs ($.00081 < P < .0055$).

Table 1: Probabilities associated with the first set of chi-square tests*

SPECIES	PROBABILITY (HO(1))*	CONCLUSION
sulfate	1.00	=> Accept HO(1)
1,1-dichloroethylene	0.0029	=> Reject HO(1)
1,1,1-trichloroethane	0.0055	=> Reject HO(1)
t-1,2-dichloroethylene	0.00081	=> Reject HO(1)

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*This set of chi-square analyses tested the following null hypothesis:

HO(1): The distribution of LOG(R) values among size classes for the chemical species in question is not different from that for chloride for all wells sampled.

$\alpha = 0.01$

In the first set of chi-square tests, significant differences among LOG(R) distributions in different wells, if present, would have inflated the corresponding chi-square values and biased the results. Thus, a second set of chi-square tests was used to compare the LOG(R) distribution of chloride against that for each of the three VOCs in each of the four wells. For all twelve tests, no significant differences were observed ($.22 < P < 1.0$). The LOG(R) distributions in Figure 6, however, suggest that the spatial variability of the organic species concentrations was, indeed, quite different from that of the inorganic species. Because of this apparent inconsistency, the inorganic and VOC data sets were pooled for a more sensitive test of the same hypothesis. Following the procedures outlined by Zar (1974), the three VOC-versus-chloride comparisons were subjected to a hetereogeneity test for each of the four wells and found to be acceptably homogeneous ($.75 < P < 1.0$).

The third set of chi-square tests, performed on the pooled chemical data (see Table 2), indicate that the inorganic species and the VOCs show significantly different degrees of spatial variability in well 37M ($P = 6.6 \times 10^{-4}$), closest to the SWC, but that the spatial variability of the VOCs approaches that of the inorganic species for all wells down-gradient from the SWC ($.18 < P < .40$). MacFarlane, et al. (1983), also found that chloride concentration-versus-depth profiles become smoother with increasing distance down-gradient from the contaminant source.

Table 2: Probabilities associated with the third set of chi-square tests*

WELL	PROBABILITY (HO(3))*	CONCLUSION
37M	0.00066	=> Reject HO(3)
38M	0.40	=> Accept HO(3)
54M	0.18	=> Accept HO(3)
21M	0.28	=> Accept HO(3)

*This set of chi-square analyses tested the following null hypothesis:

HO(3): The pooled distribution of LOG(R) among the designated size ranges for the two inorganic species is not different from that for the three VOCs in the monitoring well of interest (see text for details).

$\alpha = 0.01$

The results from the third set of chi-square analyses were corroborated by a final series of comparisons, in which the VOC data from each well were pooled and differences among wells examined. These differences were found to be significant when all four wells were included in the analysis ($P = 1.3 \times 10^{-4}$), but may not be significant when the data from well 37M were excluded ($P = 0.076$).

DISCUSSION

Three factors which may contribute to the spatial heterogeneity observed for the VOCs at the Gloucester site are the variability of sedimentary organic carbon in the aquifer solids, error introduced by the sampling and analytical procedures, and the nature of the VOC input function.

It has been widely documented (e.g., Schwarzenbach and Westall, 1981) that the concentration of sedimentary organic carbon in aquifer materials (F(oc), expressed in grams of organic carbon per gram of sediment is directly proportional to the observed partition coefficients for organic compounds when F(oc) values exceed about 0.001. Thus, one potential source of variability among VOC concentrations in the aqueous phase might be the partitioning of VOCs between the contaminated groundwater and a variable amount of sedimentary organic carbon in the aquifer matrix. At the Gloucester site, F(oc) values were found to range between 0.0012 and 0.0059, with variations among means from different depths in an individual well sometimes ranging over a factor of three (NHRI, unpublished data). Spatial variations in F(oc) at this site are therefore considerably less than what would be required to explain the observed variability in VOC concentrations.

To examine the contribution of sampling and analytical procedures to the observed spatial variability of VOC levels, we select the VOC showing the smallest degree of spatial heterogeneity—trichloroethylene—for our comparison (see Figure6). Replicate samples (with n ranging from two to six) from several points, showed coefficients of variation for trichloroethylene concentrations ranging from 0% (in 37M-19) to 23% (in 37M-6). By contrast, pairs of adjacent points in well 37M showed coefficients of variation in trichloroethylene concentrations which ranged from 6% to 130%. Sampling, analytical and temporal variability thus account for a relatively small proportion of the spatial variability observed.

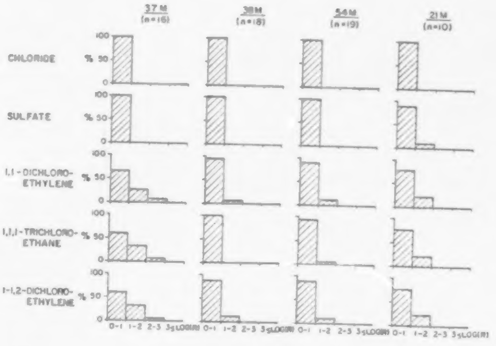

Figure 6: LOG(R) distributions for five chemical species in each of four wells. Number of points sampled in each well given in parentheses.

The spatial heterogeneity of the VOCs might also be the result of a more complex input function. The inorganic species in this system might have been gradually leached from solid refuse thereby giving rise to the smooth, regular plumes which are usually observed for inorganic ions beneath domestic landfills (e.g., Nicholson, et al., 1983). Organic solvents, on the other hand, commonly enter groundwater systems in a more erratic fashion. A sporadic input history might have given rise to the four large peaks in toluene concentration observed in 54M (see Figure 4), but it is difficult to accept that this mechanism could lead to differences in concentration exceeding two orders of magnitude between two points located one meter apart.

CONCLUSIONS

A statistical analysis of the Gloucester data has indicated that a higher density of sampling points is required to determine the spatial distribution of VOCs in contaminated groundwater than to map that of major inorganic anions with a comparable degree of confidence. In addition, the small-scale heterogeneity of the VOC levels is significantly greater near their point of entry into the flow system than further down-gradient. The aerial distribution of VOC input to most landfills is usually both highly irregular and largely unknown. Groundwater monitoring networks at impacted sites should therefore incorporate a higher density of sampling points throughout all possible input areas.

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SAMPLING ANALYTICAL CONCERNS IN VOLATILE ORGANIC CONTAMINANT STUDIES

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ABSTRACT

The choices of sampling and analytical methodologies for groundwater and subsurface processes research are frequently made from the standpoint of convenience, expediency or faith. Clearly, an optimal combination of sampling and analysis procedures must be selected to minimize errors involved in the determination of the chemical constituents of interest. Systematic errors (bias) and poor precision severely limit our understanding of net transport processes as well as the relative importance of physical, chemical or biological factors in controlling such processes. Volatile dissolved compounds are of particular interest in ground-water processes research, since they may provide valuable indicators of plume migration, inter-media transfer, solution geochemistry and microbial activity.

A systematic evaluation of ground-water sampling mechanisms has been conducted in our laboratories to determine the sources and magnitude of sample collection errors. The determination of common solution parameters (e.g., pH, Eh, Ω^{-1}, T) was unaffected by most sampling mechanisms with the exception of the peristaltic (suction) pump. The accuracy of overall determinations of dissolved gases (0_2, CH_4) and trihalomethane compounds can be significantly worsened by suction and gas displacement mechanisms. In general, mechanism related bias and imprecision are the result of degassing. Sampling error due to the mechanism of collection alone can exceed the errors involved in analytical procedures.

INTRODUCTION

Ground-water research and monitoring programs have been developed rapidly in the past four to five years. One of the primary deficiencies in many programs is the use of biased sampling procedures. The mechanisms of obtaining a representative ground-water sample have received far less attention than aspects of analytical methodology, well design and construction (Josephson, 1981; Pettyjohn, et al., 1981). The proper choice of sampling mechanism, however, may have a significant influence on sample integrity, especially volatile organics, gases and gas sensitive chemical constituents (e.g., pH, Eh, Fe, Mn, etc.). For example, systematic (determinate) errors will result from the introduction or loss of 0_2 and $C0_2$. The resultant changes in solution composition bias ground-water analytical results and may lead to serious errors in interpretations. Random (indeterminate) errors may result from the use of imprecise sample collection mechanisms or sampling difficulties in field operations. The end products of these errors are unrealiable routine monitoring or research data, a poor understanding of contamination problems, and inevitably, poor scientific or management decisions. The primary objective of this project was the identification of ground-water sampling mechanisms which provided the most reliable samples for dissolved gases and volatile organic compounds.

EXPERIMENTAL

The fourteen commercial sampling devices chosen for preliminary evaluation are shown in Table 1. They are representative of sampling devices in five mechanistic categories. Gas-lift devices employing rapid gas/water mixing to flush water out of the well, were not evaluated as they have already been documented as a biased sampling mechanism (Gibb, et al., 1981; Schuller, et al., 1981). Gas lift devices have been confused frequently with gas-displacement samplers which restrict gas/solution contact to a single interface when properly operated (Morrison and Brewer, 1981).

Table 1. Pumps

Mechanism	Type	Commercial examples
GRAB	bailer	homemade, TIMCO(R) (dual check-valve; bottom draw)
	syringe	IEA, Inc.
POSITIVE DISPLACEMENT (BLADDER, NON-GAS CONTACT)	"Middleburg" squeeze	IEA, Inc. (Aquarius); QED Corp. (Well Wizard), Timco (GFP-TRV-2558)
	bladder inflation	ISCO(R) (#2600)

POSITIVE DISPLACEMENT (MECHANICAL)	helical rotor
	reciprocating diaphragm
		Johnson Div. (UOP) - Keck, #SP-81
		Bennett(R) (#180)

GAS DISPLACEMENT (GAS CONTACT)	dedicated or pressure lysimeter type	Barcad(R) TIMCO(R) (GFP-TTVPLS-2474)
OTHER	venturi suction (peristaltic)	ECO(R) (Samplifier) Masterflex(R) (#7570)

Two levels of testing were conducted to evaluate the sampling mechanisms. The first level of testing dealt with the effect on solution parameters (pH, Eh, conductivity - Ω^{-1}, and temperature - T) and gases (0_2, CH_4). These tests were conducted in a hydrologic test well facility in which buffered tap water (pH 7.5-8), equilibrated with an appropriate gas mixture, was circulated under controlled conditions. The testing system simulated 9.2 m of lift and 5.0 m of head above the sampler. Each device was sampled in triplicate while background solution samples (control samples) were taken simultaneously from a sampling port in the test well. Solution parameters were measured with a flow-through electrode device, while 0_2 and CH_4 were determined by Winkler titration and flame ionization GC, respectively.

The second level of testing determined the effect of the sampling mechanism on the precision and accuracy of trihalomethane (THM) compound analytical results. The devices were operated in a 22-liter closed-system cell under the same conditions of head and lift described above. The background tap water solution was spiked with the THM's at concentrations ranging from 80-8000 µg/L total THM's. As before, triplicate samples were collected from each device and analyzed along with control samples, control standards and blanks. The THM's were analyzed by the purge-and-trap technique outlined in EPA Method 601. Details of the experimental design and results are provided in Barcelona, et al. (1984).

RESULTS

Solution Parameters (pH, Eh, Ω^{-1}, T)

Measurement precision levels for the solution parameters were determined to be: ±0.01 pH units, ±2 mv (Eh), ±5 µS (Ω^{-1}) and ±0.1 C°. A significant deviation was determined to be five times these levels.

The most sensitive parameters to the choice of pumping mechanism were pH and Eh. No significant deviations were noted in conductivity or temperature for any of the devices. Only the peristaltic mechanism exhibited significant changes in pH and Eh relative to the controls. Average changes were +0.05 pH units and −20 mv Eh, which are the expected changes from degassing $C0_2$ and 0_2 from the solution.

O_2 and CH_4 Exchange

The tests evaluating 0_2 and CH_4 exchange were conducted in the ranges of 2-6 mg $0_2 \cdot L^{-1}$ and 0.1-18 mg $CH_4 \cdot L^{-1}$. The accuracy and precision for control samples and standards indicated that the testing protocol was capable of discriminating systematic sampling biases from corresponding analytical error.

The performance of eleven commercial devices in five mechanistic categories is shown in Tables 2 and 3. The accuracy of analytical results on water samples collected by the various mechanisms was uniformly poorer than that observed for the control samples. In most cases the bias introduced by the sampling mechanism was in a range from −1 to −24% from the mean control values. This means that exchange or loss of gaseous solutes can be expected to cause false low values even in carefully collected ground-water samples. The use of the positive

Table 2. Average Accuracy of Results from Device Collected Samples Relative to Control Samples

	Oxygen Recovery/Addition		Methane Recovery		Overall accuracy	
	% Bias*	(N)**	% Bias	(N)	% Bias	(N)
POSITIVE DISPLACEMENT (bladder, no gas contact, 3 designs)	-3	(3)	-15	(4)	-10	(7)
GRAB SAMPLING						
Conventional Bailer	**-8.5**∇	**(3)**	**-35**	**(1)**	**-12**	**(4)**
Dual-check valve bailer	-13.5	(3)	-6.8	(1)	-12	(4)
Syringe sampler	**-7.0**	**(3)**	**-20**	**(1)**	**-10**	**(4)**
GAS-DISPLACEMENT (2 designs)	**+9**	**(3)**	**-18**	**(4)**	**-12**Δ	**(6)**
SUCTION (1 design)	**-8**	**(1)**	**-23**	**(2)**	**-18**	**(3)**
POSITIVE DISPLACEMENT (mechanical, 2 designs)	**-13**	**(4)**	**-36**	**(4)**	**-24**	**(8)**
CONTROL SAMPLES	-1	(4)	-8	(9)	-7	(13)

* % Bias - Average percent bias for the category.

** (N) - Number of individual experimental runs. Each device was run with triplicate samples, control samples and calibration standards.

∇ Bold entries denote significant differences were observed in more than half the experimental runs at the 95% confidence interval from Students "t" test.

Δ Overall accuracy cannot be reasonably assessed, since gross oxygen addition was observed in one run due to a check-valve malfunction which resulted in a high positive average bias. Discounting this value, the overall accuracy was statistically identical to the conventional bailer results.

displacement (no gas contact) pumps (operated with air or N_2) and the grab mechanisms tended to minimize losses of oxygen and methane when carefully operated under controlled conditions. Gas displacement devices provided reasonably accurate results with the exception of oxygen sensitive constituents when air was used as the drive gas. Only the bladder pumps and the dual check valve, bottom draw bailer sample results were not significantly different from the control mean values. This was a direct consequence of sampling precision (Table 3) which limited statistical tests (e.g. Student's "t" test) of mechanism related errors. The data in Table 3 clearly show that the precision of samples collected by most of the devices was poorer by a factor of two or more than that of the control samples.

Table 3. Average Precision of Results from Device Collected Samples Relative to Control Samples

	Oxygen $\frac{RSD_s}{RSD_c}$	Methane $\frac{RSD_s}{RSD_c}$
POSITIVE DISPLACEMENT (bladder)	1	1
GRAB SAMPLES		
Conventional bailer	1	1
Dual-check valve bailer	4	2
Syringe sampler	3	3
POSITIVE DISPLACEMENT (mechanical)	3	1
GAS DISPLACEMENT	4	3
SUCTION	4	1

* Ratio of the relative standard deviation (RSD) of the samples from the devices to the RSD of the control samples.

The level two evaluation illustrated two major points. Inaccurate results (negative bias) can occur, from sampling mechanism effects alone, which are 2 to 3 times higher than analytical bias. Poor precision arises from the actual operating conditions during sample collection. In this respect, the sampling mechanism and the expertise of the sampling technician are the major sources of imprecision.

Precision and Accuracy of THM Samples

At least one device in each of the mechanistic categories shown in Tables 2 and 3, except for the mechanical positive displacement pumps, was evaluated for precision and accuracy (recovery) in sampling the THM solutions. The analytical performance data in Table 4 demonstrate that method performance for the four purgeable trihalomethane analyses was more than adequate to evaluate the effects of sampling mechanism related errors. The accuracy and precision of both the calibration standards and control samples was better than 90% and 5%, respectively. Since analytical procedures and sample handling methods were identical for each mechanism and parallel control samples, the effect of mechanism related error alone was isolated.

Table 4. Accuracy and Precision of Controls

Compound		$CHCl_3$		$CHBrCl_2$		$CHClBr_2$		$CHBr_3$		Total THMS	
		Percent									
N	Type of Control	Bias	RSD	Bias	RSD	Bias	RSD	Bias	RSD	Bias	RSD
(611)	Samples* (20-2,000 ppb)	*	4.0	*	3.5	*	2.6	*	2.1	*	2.7
(80)	Calibration Standards** (10-2,000 ppb)	NA	4.7	NA	3.8	NA	3.9	NA	3.6	-9.9	4.4
(5)	Procedural Standards*** (4.5-68.3 ppb)	-9.5	5.4	-15	5.8	-9.7	9.9	+13.5	15.5	-6.8	11.6

* Control samples were taken as the true values for comparison purposes.

** Standards used daily to establish relative response factors (RRF) for each compound relative to dichlorobutane internal standard; criterion for acceptance was ±10% from the RRF range established by procedural standards.

*** Method procedural standards run at intervals during the four-month study to evaluate the stability of the methodology

N - Denotes the number of samples run in duplicate.

NA- Not applicable

The accuracy and precision of the sampling runs for each mechanism at three levels of THM mixture concentration are shown in Table 5. Relative to the control samples, the positive displacement bladder pumps and the bailers showed no significant differences in accuracy or precision. With reference to the bailers, it should be noted that grab samples were taken directly from the reservoir and the samples were not subjected to the typical disturbance of samples involved in retrieving the bailer from depth in a well-bore. The results are indicative therefore of optimum sampling conditions and should not be considered typical of field performance. There was an indication in the data that the dual check valve bailer gave somewhat better overall recovery than the conventional bailer, but the difference was not statistically significant.

Table 5. Average Accuracy and Precision of Results from Sampling Devices Relative to Controls*

	Total THM Levels (ppb)					
	80-150		700-1000		2,000-8,000	
Sampling Device	% Bias	RSD sample / RSD control	% Bias	RSD sample / RSD control	% Bias	RSD sample / RSD control
POSITIVE DISPLACEMENT (bladder)	-0.9	0.6	-1.3	0.1	<0.1	0.8
GRAB SAMPLERS						
Conv. bailer	-2.2	0.[illegible]	-0.4	0.7	-0.9	2.5
Dual-check valve bottom draw bailer	+0.8	1.5	+0.8	1.2	+1.7	0.6
GAS DISPLACEMENT	-7.7**	**1.6**	-3.2	1.4	**-5.5**	**0.4**
SUCTION	**-4.1**	**0.8**	**-14.8**	**0.7**	**-16.1**	**0.3**

* At least eighteen samples and control samples were run at each concentration level for each device.

** Bold entries denote statistically significant differences from controls at the 99% level.

In general, the observed precision of the devices and control samples was sufficient to permit the treatment of the data by Student's "t" statistic. This was not the case in the first level test results where the variances were judged statistically different by the variance ratio (F) test.

The gas displacement and the peristaltic pump results clearly show that statistically significant losses or purgeable organic compounds can occur due to mechanism effects even under controlled sampling conditions. In most cases the bias worsened as the total concentration of THM's increased. The effects observed for the peristaltic (suction) mechanism are further supported by the recent work of Ho (1983), who evaluated the effects of lift, concentration and materials on purgeable compound recoveries. He observed strongly negative biased recoveries ranging from 5 to 8 percent for THM compounds at lifts of 8 to 16 feet. These values are in excellent agreement with the value of −4.1% bias at 12 ft lift observed in this study in the low concentration range. It may be expected that ground-water sampling for the determination of volatile organic compounds with either gas displacement or suction mechanisms will introduce significant error into monitoring results. Sampling mechanisms' effects under field conditions may be much greater, particularly for the conventional single check valve bailer, gas displacement and peristaltic pumps. These devices demand very careful control of operating variables: agitation, pressurization/depressurization cycles and flow rate, which may complicate sample retrieval. These observations underscore the need for careful selection of sampling mechanisms and methods in ground-water monitoring efforts in order to insure the reliable collection of representative samples.

In summary, the overall performance ranking of commercial sampling mechanisms is shown in Table 6 with recommendations for use. It is presented as guide for planning comprehensive ground-water data collection efforts. It should be reiterated that a careful evaluation of the information needs of the ground-water monitoring program must be conducted prior to deciding on sampling mechanisms and protocols.

Table 6. Performance Evaluation of Ground-Water Sampling Mechanisms For Purgeable and Gas Sensitive Parameters

Mechanism category	Overall performance ranking	Remarks
POSITIVE DISPLACEMENT (bladder)	Above average	Expected to provide both efficient well-purging and representative samples over a range of conditions with minimal difficulty in field operations
GRAB SAMPLES		
Conventional bailer	Average	Unsuitable for well-purging; require very careful operation and sample handling precautions under field conditions; field performance open to question
Dual-check valve bailer	Average	
Syringe pump	Average - below average	
POSITIVE DISPLACEMENT (mechanical)	Average - below average	Suitable for well purging; sampling performance very dependent on specific design and operational details
GAS DISPLACEMENT (gas drive, not gas lift)	Average - below average	May be suitable for well purging if used in conventional installations; malfunctions are difficult to assess or repair; significantly lower recoveries of purgeable organic compounds and gases may occur depending on field conditions and operator experience.
SUCTION	Below average	Suitable for well purging at depths to approximately 20 feet; significantly lower recoveries of purgeable organic compounds and gases will result from sampling with this mechanism.

CONCLUSIONS

The task of obtaining representative samples of ground water in both research and compliance monitoring programs must be carefully approached. Most pumping mechanisms may be expected to perform satisfactorily for well purging and the measurement of solution parameters. However, sampling for gas-sensitive and volatile chemical constituents can be significantly biased by degassing and loss of volatiles during sample collection.

Significant bias and poor precision may be expected in shallow ground-water sampling with gas displacement, positive displacement mechanical and suction mechanisms, unless extraordinary care is taken in sample retrieval, transfer and collection. Bladder (no-gas contact) pumps are superior for most applications. The performance of grab samplers, particularly bailers, is heavily dependent on both the expertise of sampling personnel and field conditions. The ideal controlled conditions under which these performance data were collected represent an optimum situation for the observance of minimal sampling error. Field conditions and solution composition are complicating factors which must be evaluated on a case by case basis.

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USE OF THE ELECTRICAL POTENTIAL OF CELL MEMBRANES TO RAPIDLY ASSESS POTENTIAL TOXICANTS

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ABSTRACT

Isolated frog skin retains most of its in-vivo function for 24 hours. One of the in-vitro functions is to actively transport Na from the pond-side of the skin to the blood-side. Since many toxicants are lipid-soluble or affect the characteristics of membranes, we have chosen to test if the Electrical Potential Difference and Short-Circuit Current of the Frog skin is a useful assay system for rapid determinations of effects of membrane-active toxicants. Naphthalene was used to assess the feasibility of the system to detect the effect of toxicants on the active transport parameters of epithelia vertebrates. The Potential Difference (PD) and Short-Circuit Current (SCC) were used as indicators of the net movement of Sodium, activity of the Sodium-Potassium pump, and the conductivity of the para-cellular leakage pathways.

Naphthalene was found to alter the membrane potential and short-circuit current of the frog skin with a linear relationship. Using naphthalene concentrations in the 1 to 10 mg/L range, naphthalene was found to cause rapid increase in the Short-Circuit Current, the measure of Active Sodium Transport. I conclude then that the Short-Circuit Current is a viable assay method for rapid determination of toxicant effects.

INTRODUCTION

The toxicity of PAH (Polycyclic Aromatic Hydrocarbons) to organisms is well documented. One of the effects of PAH compounds is to modify the ion concentrations of blood/hemolymph in the tested organisms. This effect has been documented in bacteria (Bernheim, 1974), green algae (Kauss and Hutchinson, 1977), fish (Levitan and Taylor, 1979), and freshwater invertebrates (Darville et al., 1983). Since the establishment and maintenance of ionic gradients is due to the action of various ion "pumps" or active transport systems, the measurement of the pump's activity should be a valuable assay tool to discern the potential toxicity of a compound. This study will attempt to validate the feasibility of using the trans-epithelial Electrical Potential Difference (TEP) and Short-Circuit Current (SCC), which is the measure of net Na active transport rate, entry pathways for Na, and the state of the para-cellular pathways.

I have chosen to use the skin of the frog, *Rana pipiens*, as an assay system for this initial effort. Frog skin has been the favorite experimental tool for studying active Na ion transport for almost thirty years (Koefoed-Johnsen and Ussing, 1957). In the frog skin, the high rate of Na active transport and the identity between Na active transport and the SCC make the frog skin suitable for assessing the action of toxicants. Also since the frog skin is the model epithelial ion transport system (e.g. embryonic human skin actively transports Na) and is an epithelium rather than a collection of single cells results obtained with the frog skin will have a wide applicability to vertebrate/mammalian epithelia. In particular, it is epithelia, rather than single cells, that build and maintain the ionic gradients that exist between organisms and the environment.

MATERIALS AND METHODS

Healthy, unsexed, adult *Rana pipiens* were obtained from Carolina Biological (usual source). Frogs were anesthesized and the abdominal skin removed and mounted on a chamber (modified Ussing) which has two fluid compartments separated by the frog skin. These fluid compartments are stirred and aerated by a gas lift pump, one for each compartment. With this pump system solution changes can be made rapidly and without altering the hydrostatic pressure on the frog skin (Wood and Moreton, 1979). In the bathing solutions are salt bridges, made of 3% Agar Noble-Frog Ringer solutions that transmit the Electrical Potential Difference (TEP) from the frog skin to Calomel Cells (A.H. Thomas) that convert the ionic TEP to wires. The signal from the Calomel cells is acquired through Voltage Follower circuits in a Voltage Clamp, a device that is capable of maintaining a particular voltage across the frog skin. If the maintained voltage across the frog skin is zero volts and identical bathing solutions are used on each side of the skin, the frog skin is said to be short-circuited. At the short circuit condition the current required to maintain zero TEP exactly measures the net ion flux across the frog skin. In the frog skin, but not in all other Na epithelia, the SCC is identical to the net Na flux thus permitting us to use the SCC as the measure of the rate of Na active transport by the Na "pump". The measurement of the TEP detects changes in both the pump rate and in the state of the para-cellular pathway between the cells. SCC is applied with silver plates located in the bathing solution on each side of the frog skin. SCC was traced on Linear chart recorders. Supportive measurements of TEP and SCC were taken from the Voltage Clamp which was calibrated with a Keithley Electrometer.

Control and test solutions were made as follows: 110 mM NaCl, 2.5 mM KC1, 1 mM Tris, 1 mM CaC12 and 1% ethanol (V/V) adjusted to pH 8 (called Ethanol Ringer's in text). Naphthalene was dissolved in ethanol before being added to the test solution. The water used to make solutions was glass distilled from a deionized source.

Experimental protocol was to first "equilibrate" the mounted frog skin for a half hour in ethanol ringers, then change the solution to the test solution for one-half hour, then changed back to the Ethanol-Ringer's. Data was analyzed as Test SCC minus Control SCC.

RESULTS

Data from the experiments will be presented in "raw" and in tabular form. The raw data consists of chart recorder tracings of SCC vs. time. Fig. 1 is the raw data from an experiment in which the ethanol bathing solution was used for the first thirty minutes. At the thirty

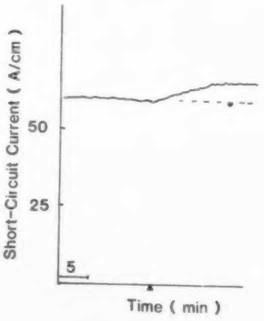

FIG. 1 FROG SKIN SHORT-CIRCUIT CURRENT vs. TIME

Tracing of a chart recorder record in which the initial bathing solution was ethanol-Ringer's. The record is of the short-circuit current against time. At the 15 minute mark, the bathing solution was changed to ethanol Ringer's with 5 mg/L Naphthalene. The SCC (short circuit current then increased.

minute mark, the serosal bathing solution was changed to iso-osmotic bathing solution with 10 mg/L of naphthalene added. When the blood-side bathing solution was changed to Naphthalene-Ringer's, the SCC rose from 40 uA/Cm^2 to 50 uA/cm^2. Replacement of the naphthalene bathing solution with ethanol Ringer's causes a trend to return to the original values of SCC and TEP. This data implies that the effect of naphthalene on the frog skin is reversible. Fig. 1 is typical of the experiments that were done with varying concentrations of naphthalene. Fig. 2 is the collection of SCC data plotted against the naphthalene concentration. Examination of the figure shows that the naphthalene concentration on SCC is highly correlated with the SCC. The regression coefficient is 0.99.

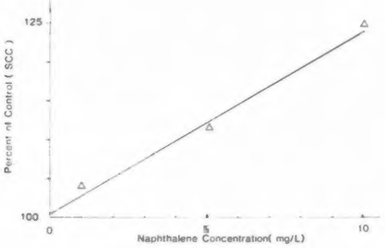

FIG. 2 FROG SKIN SHORT-CIRCUIT CURRENT vs. NAPHTHALENE CONCENTRATION

Plot of groups of experiments in which the SCC was recorded vs. time. Those experimental experiments were grouped and the average plotted against the naphthalene concentration in the bathing solution. The line is the linear regression of the SCC on the naphthalene concentration.

Table I is a collection of the data from all of the naphthalene points collected for the frog skins. The results in the Table show that naphthalene has a significant effect on the SCC compared to the ethanol control for all naphthalene values.

TABLE I

EFFECT OF NAPTHALENE ON ACTIVE TRANSPORT RATES IN THE FROG SKIN

NAPTHALENE CONCENTRATION	PERCENT INCREASE IN ACTIVE TRANSPORT
1 mg/l	4.1 ± 1.3$_a$
5 mg/l	11.8 ± 2.3$_a$
10 mg/l	23.6 ± 3.2$_a$

$_a$% increase in scc (short-circuit current) - control SCC ± s.d.

DISCUSSION

The results presented in this paper show that the reaction of the SCC to naphthalene is very rapid and has a linear relationship to the amount of naphthalene applied. At the end of five minutes the naphthalene has modified the capacity of the frog skin to actively transport Na ions as evidenced by the significant increase in the SCC after treatment with naphthalene. The rapid response of these epithelial parameters to naphthalene imply that the frog skin is a useful indicator of the effect of naphthalene on active transport and has strong possibilities as a rapid indicator screen for suspected membrane-active toxicants.

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IN-SITU DETERMINATION OF DISPERSION COEFFICIENTS AND ADSORPTION PARAMETERS FOR CONTAMINANTS USING A PUSH-PULL TEST

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ABSTRACT

This paper describes a practical in-situ test procedures for measuring dispersion coefficients and adsorption parameters. The procedure involves injection of a relatively small volume of groundwater spiked with the solute of interest and subsequent production of fluid. Laboratory experiments are required to define the form of the adsorption equation, and to determine the volume and concentrations to be injected. The dispersion coefficient is determined by history-matching the effluent composition of a non-adsorbing species, for which total anions is an alternative, against the computer results. The adsorption parameters are then determined by history-matching the effluent composition against the computer results. A computer program has been developed which uses any one of several adsorption equations. A boundary condition used in previous studies is shown to be in error, and the correct boundary condition is presented.

INTRODUCTION

The problems associated with migration of contaminants in near-surface aquifers have received a great deal of attention in recent years. The sources of contaminants include leaching or leakage from surface disposal sites, accidental spills, leaks from underground tanks or pipes, and injection wells for industrial wastes and in-situ mineral recovery. The contaminants include a wide range of organic and inorganic compounds and metals. If contamination problems are to be handled effectively, it is essential to be able to predict the rates at which various contaminants will migrate in the subsurface and the effectiveness of possible cleanup procedures.

The parameters that largely determine the extent to which contaminants migrate, and the extent to which cleanup is feasible, include groundwater velocity, permeabilities, heterogeneities, dispersion parameters, adsorption parameters, and the availability of reactants and organisms. A review of contaminant migration is given by Gillham and Cherry (1982) and Anderson (1979). Methods to determine these parameters have been proposed by many investigators; however, the methods to determine dispersion and adsorption parameters are based either on laboratory experiments or multi-well field techniques. It is uncertain whether laboratory-measured parameters are representative of field situations, and multi-well techniques are expensive and difficult to interpret unambiguously. In this paper we describe a field test procedure for measuring dispersion and adsorption parameters in an aquifer. The general approach is the same for all solutes, organic or inorganic, provided an immiscible liquid does not form and there are no significant losses due to volatilization.

The directional permeability is estimated using standard pump test techniques (see, e.g., Way and McKee, 1982). Sometimes areal heterogeneities can also be detected from these tests. Permeability as a function of depth can be measured using spinner flow logging or analyzing core samples in the laboratory. Natural groundwater velocity and direction can then be easily determined from potential head measurements at a number of locations.

BACKGROUND ON DISPERSION

The mixing of miscible fluids as they flow through granular media is called dispersion. On a microscopic scale mixing of fluids occurs due to molecular diffusion and microscopic variations in flow velocity. In the aquifer systems of concern, molecular diffusion is negligible compared to the mixing due to velocity variations resulting from pore size distribution, pore geometry, and dead-end pore spaces.

Dispersion is quantified through the use of the coefficient of dispersion. It is known that the coefficient of dispersion is proportional to the velocity (Anderson, 1979) and the coefficient of proportionality is known as dispersivity. Dispersion occurring in the direction of mean flow is termed longitudinal dispersion, and that which is occurring perpendicular to the direction of mean flow is termed transverse dispersion. It is commonly assumed (e.g., Bredehoeft and Pinder, 1973; Konikow and Bredehoeft, 1974) that transverse dispersivity is about 30% of longitudinal dispersivity. Dispersivity obtained using fracture frequency (Way and McKee, 1981) suggests that transverse dispersivity is about 20-40% of longitudinal dispersivity. The magnitude of measured dispersivity changes depending on the scale at which the measurements are taken (Fried, 1975; Cole, 1972). Laboratory experiments yield values in the range of 10^{-2} to 1 cm, while dispersivities of up to 100 m have been obtained for field problems (Anderson, 1979). Multi-well injection-production with or without observation wells (Grove and Beetem, 1971; Kaufman, 1960), single-well injection with observation wells (Calmels et al., 1979; Goblet et al., 1979; Pickens et al., 1981), and the single-well pulse technique (Fried, 1975) have been used to determine dispersivity. Calculated dispersivity values depend on the way in which samples are collected and the amount of aquifer sampled (scale).

Drever and McKee (1980) used single-well injection and subsequent recovery (the push-pull test) to obtain adsorption parameters in the absence of dispersion. Kabir et al. (1982) extended the idea to include the effect of dispersion; the boundary conditions they used, however, are only approximations.

BACKGROUND ON ADSORPTION

Adsorption of Ions

The migration of solutes is affected by chemical reaction. Possible types of reaction include precipitation or coprecipitation, biodegradation, and adsorption onto the solid materials of the aquifer. In many, if not most, instances of contaminant migration, adsorption is the only significant chemical process. Qualitatively, adsorption has two major effects: it causes the migration of an adsorbed species to be retarded, and it makes complete removal of the contaminant from the aquifer—by, for example, prolonged flushing with clean water—extremely slow if not impossible. Availability of some reactants can be determined using two-well injection-recovery tests (paper in preparation).

The most complete description of adsorption of ions by oxide-type surfaces is that of Davis et al (1978), which considers variable surface charge, chemical interactions, and speciation explicitly. The model is, however, too detailed and requires too many parameters to be measured for the practical applications we are discussing here. Various simplifying assumptions can be made to give equations that are suitable for practical applications.

Selectivity Coefficient

Exchange between two monovalent cations, A^+ and B^+, can be described by an equation

$$[\frac{y_A}{y_B}]^n = K'_{AB} \frac{C_A}{C_B} , \tag{1}$$

where y represents the adsorbed concentration (meq/kg), C the concentration in solution (meq/kg), and K_{AB} is the selectivity coefficient.

The exponent n allows for non-ideality effects; n is often set equal to 1 for simplicity. The analogous equation for monovalent-divalent exchange is

$$[\frac{y_A^2}{y_B}]^n = K'_{AB}\,\frac{C_A^2}{C_{B^2}}\ . \qquad (2)$$

As a further simplification, if only one cation (A^+) is of interest, the remaining cations can sometimes be treated as a single monovalent cation, M^+ (Drever and McKee, 1980). Equation (1) becomes, setting $n = 1$,

$$\frac{y_A}{y_M} = K'_x\,\frac{C_A}{C_M}\ . \qquad (3)$$

If the total concentration of cations in solution is C_a ($C_a = C_A + C_M$), and the cation exchange capacity of the solid, CEC, is constant, then Eq. 3 becomes

$$y_A = K'_x\ \mathrm{CEC}\,\frac{C_A}{C_a + (K'_x - 1)\ C_A}\ . \qquad (4)$$

The Distribution Coefficient

If the species A is present in trace concentrations only, then $C_A << C_a$ and $y_A << \mathrm{CEC}$. If C_a is constant, Eq. 4 reduces to

$$y_A = K_d\ C_A\ , \qquad (5)$$

where K_d is the distribution coefficient ($= K'_x\ \mathrm{CEC}/C_a$). Eq. 5 can be modified for non-ideality by

$$y_A = K_d\ C_A^n\ , \qquad (6)$$

where n is an empirical constant. Eq. 6 is a form of the well-known Freundlich isotherm.

Adsorption of Uncharged Species

Uncharged species, which are most commonly organic molecules, may also be adsorbed by the minerals and solid organic matter in an aquifer (McCarty et al., 1981). The adsorption may or may not be readily reversible. If it is reversible, it can often be described by the Freundlich isotherm (Eq. 6) in the low-concentration regime, or by the Langmuir isotherm, which is analogous to Eq. 4, when the adsorbate is present in high concentrations.

Adsorption can thus be modeled by several different mathematical equations, and each requires at least one parameter to be known or measured. It is unrealistic to expect that the form of the appropriate equation and the values of several parameters can be measured in a single push-pull test. It is our experience that laboratory experiments using sediment and groundwater from the field site are necessary to define the form of the adsorption equation (i.e., which of Eqs. 1 through 6 best describes and adsorption behavior observed in the laboratory) and to determine a value for the exponent n in Eqs. 1, 2, or 6, if such an exponent is necessary. It is also useful to measure the cation exchange capacity and selectivity coefficient (or equivalent constant) in the laboratory as a guide to planning the push-pull test, although the test results themselves are used to give the in-situ values for these parameters. The laboratory experiments reduce the number of parameters to be measured by the push-pull test, and define the most appropriate form of adsorption equation for modeling contaminant transport.

THE PUSH-PULL TEST

The push-pull test, a relatively simple concept, involves injection of an appropriate amount of groundwater spiked with solutes of interest and subsequent production of a large volume of fluids. Figure 1 shows the test arrangements. A single fully penetrating water well is drilled and cased. Water from the well is filtered and stored into an easily erected pool or bladder. Appropriate amounts of solutes to be studied are mixed with the formation water and injected into the formation and allowed to reside (soak) for a predetermined period of time. A pump is then lowered into the well to recover the solution, and the resulting concentration is measured as a function of volume produced. Subsequent production without a soaking period causes a sudden reversal of the flow, and thus results in unpredictable mixing and therefore a misleading dispersivity. Since the analysis to follow assumes a steady flow field, we recommend that formation fluid without solutes be injected for some time before solute spiked with groundwater is injected.

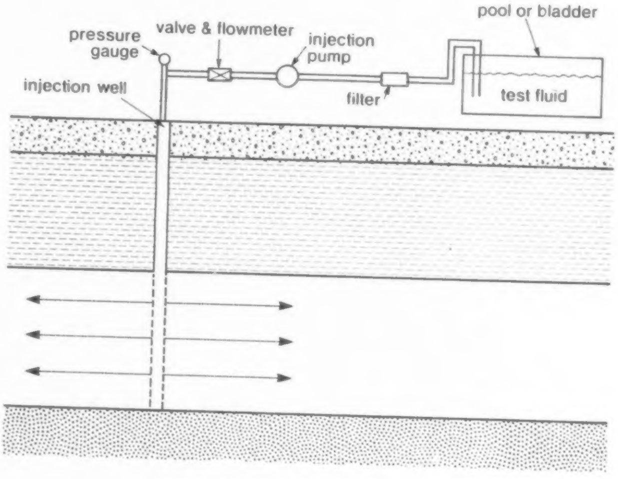

Figure 1. Layout of Push-Pull Test

Typically, 15,000 to 20,000 liters of solution are injected and about 10-12 times this amount is recovered. If the aquifer porosity is about 30%, the push-pull test would test approximately 100 metric tons of sediment. In the case of coal and other tight formations with fracture porosity on the order of a few percent, approximately 1000 metric tons of coal would be exposed to solution. This is in comparison to a few grams to kilograms tested in laboratory experiments. The test has another advantage in that it is relatively easy to obtain the necessary permits (Drever and McKee, 1980), in contrast to other field methods.

THE MATHEMATICAL MODEL

The following assumptions and idealizations have been made in development of the model:

1. The porous medium is macroscopically uniform, i.e., permeability and porosity are constant.
2. Mobilities of injected and formation fluids are equal.
3. The fluid is both single-phase and incompressible—i.e., the velocity field is at steady-state conditions.
4. An instant equilibrium exists between moving fluid and a single stationary phase (solids).

As noted earlier, for demonstration purposes we will use the constant CEC model, although other models are included in the computer program. Models not listed here can also be easily incorporated.

Units of y_1 (Eq. 4) are meq/kg solid and the cation of interest is denoted by the subscript "1". When units of y_1 are converted from meq/kg solid to meq/kg liquid (q_1), the equilibrium relationship applicable to a binary cation exchange (Eq. 4) can be written as

$$q_1 = \frac{(1-\phi)\rho_S \, K_x' \cdot CEC}{\phi \rho_\ell} \; \frac{C_1}{C_a + (K_x' - 1)C_1} \, , \tag{7}$$

where ϕ is porosity, and ρ_S and ρ_ℓ are solid and liquid densities, respectively.

The conservation of mass equation for cation 1 is given by

$$-\frac{Q}{2\pi rh}\frac{\partial C_1}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\left(D \, r \frac{\partial C_1}{\partial r}\right) = \phi \frac{\partial}{\partial t}(C_1 + q_1), \tag{8}$$

where

$$D = \frac{D_o}{F} + \alpha_\ell \left|\frac{Q}{2\pi rn}\right| = \alpha_\ell \left|\frac{Q}{2\pi rh}\right| ,$$

h is the formation thickness, and α_ℓ is longitudinal dispersivity. Notice that the contribution from molecular diffusion (D_o/F) has been neglected. As noted earlier, this is a good practical approximation. The flow rate, Q, is considered positive for injection and negative for production.

The conservation of mass equation for total anions is, similarly, given by

$$-\frac{Q}{2\pi rh}\frac{\partial C_a}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}\left(D \, r \frac{\partial C_a}{\partial r}\right) = \phi \frac{\partial C_a}{\partial t} \tag{9}$$

These equations must satisfy the following initial condition

$$C_a = C_a^{GW} \text{ and } C_1 = C_1^{GW} \text{ at } t = 0, \tag{10a}$$

and boundary conditions for $t > 0$ are

$$C_a = C_a^{GW} \text{ and } C_1 = C_1^{GW} \text{ at } r \to \infty \, , \tag{10b}$$

and for the push as well as pull cycles

$$J_{r_w^-} = J_{r_w^+} \text{ at the well,} \tag{10c}$$

which simplifies for the pull cycle to

$$\frac{\partial C_a}{\partial r} = \frac{\partial C_1}{\partial r} = 0 \text{ at } r = r_w \, .$$

The first boundary condition says that concentration does not change far from the well, and the second equates mass fluxes at the face of the well. Gupta and Greenkorn (1976) and Kabir et al. (1982) use $C = C^I$ at $r = r_w$ for the push cycle. This approximation is valid only after a long time (Bear, 1972), and it does not conserve mass. If very large volumes are injected, such that r_A (Eq. 11b) is very large compared to r_w, then the approximation does not affect overall results.

The following dimensionless variables are defined to simplify the equations for the computer model:

$$T = (t/t_I) \, |Q/Q_I| \quad \text{and} \quad x = r^2/r_A^2 \, , \tag{11a}$$

where

$$r_A^2 = \frac{Q_I t_I}{\pi h \phi} \tag{11b}$$

A generalized finite-difference computer model was developed that will take backward-in-distance, forward-in-distance, or center-in-distance, along with backward-in-time, forward-in-time, or center-in-time differencing schemes.

Notice that Eqs. 8 and 9 are nonlinear; therefore they are solved with successive substitutions. The steps are automatically controlled to allow a maximum of 2% change in concentration per step.

RESULTS

Production histories of total anions and the cation of interest are needed to determine dispersivity and adsorption parameters. The appropriate adsorption equation is selected on the basis of laboratory experiments. The production history of total anions is first matched with model-predicted curves in order to define the dispersivity. Once the dispersivity is known, the cation production history is matched with predicted curves in order to estimate the adsorption parameters. This procedure is illustrated using data from push-pull tests conducted in the bottom two meters of a gravel aquifer containing varying amounts (2%-21%) of clay. Two push-pull tests were conducted: In the first, 9780 liters of groundwater spiked with 1070 mg NH_3 per liter as ammonium carbonate were injected. In the second test, 9200 liters of groundwater spiked with ammonium carbonate (1140 mg NH_3 per liter) and oxygen were injected.

Figure 2 shows the concentration produced as a function of the number of pore volumes recovered. The dashed line represents a break

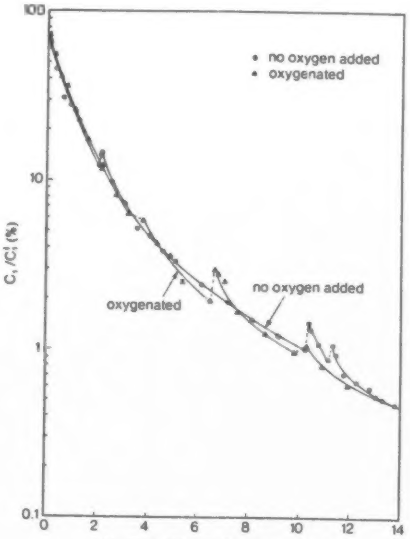

Figure 2. Ammonia production history.

in pumping. The break in pumping disturbs the velocity, which cannot be handled by this model. It also represents unpredictable dead-end pore effects. The production history shows that production concentrations are always less than the injection concentration; therefore the approximate boundary conditions widely used in previous studies are not appropriate in this case.

Dispersivity

Unfortunately, anions were not measured in these tests. However, another push-pull test was conducted using Amino G acid as a tracer dye. Laboratory experiments showed that this dye does not absorb, and consequently tracer dye production history can be used to determine dispersivity. About 5000 liters of formation water spiked with 9.8 ppm tracer dye were injected, and reliable dye concentrations were obtained during production of 27,000 liters (Fig. 3). On the basis of predicted curves based on the model, the best value for longitudinal dispersivity is 0.4 m. Since dispersivities depend on the linear distance sampled, and a larger volume was injected in the ammonia tests, a longitudinal dispersivity of 0.6 m will also be used as an upper limit for dispersivity in estimating adsorption parameters.

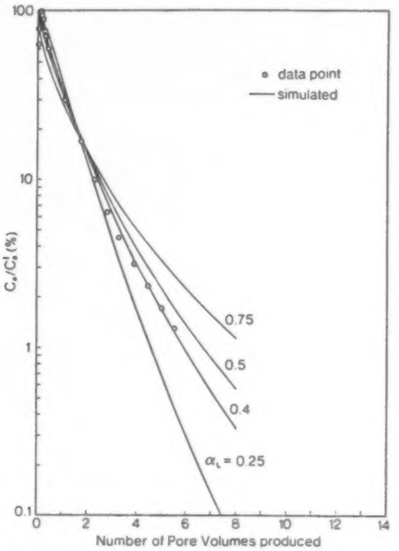

Figure 3. Tracer dye production history compared to simulated history for various values of longitudinal dispersivity

Adsorption Parameters

No laboratory experiments were performed on the cores from this aquifer to determine the form of the adsorption equation. However, Drever and McKee (1980) showed that the constant CEC model adequately described ammonia adsorption in another aquifer, and that model is used here. The model results in a good fit to production history (Fig. 4). The best fit for α_L = 0.4 m is obtained for a value of CEC = 2.25 meq/100 g and K'_x = 0.5. While Figure 4 shows the effect of varying CEC at fixed K'_x on production history, Figure 5 shows the effect of varying K'_x at fixed CEC. As expected, the higher the CEC or K'_x, the longer the time required to restore the aquifer to its original condition. Figures 4 and 5 also show that most of the information on adsorption parameters is contained in the later part of the production history. It is therefore not surprising that Kabir et al. (1982) had difficulties in obtaining adsorption parameters by plotting data for less than 1.5 pore volumes recovered. Reliable values of adsorption parameters cannot be predicted using this part of the data only.

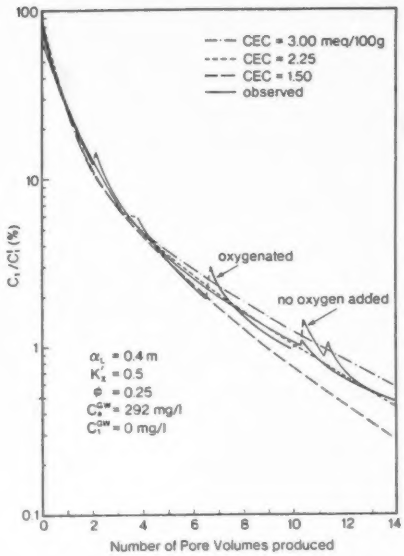

Figure 4. Ammonia production history compared to simulated history for various values of Cation Exchange Capacity (CEC)

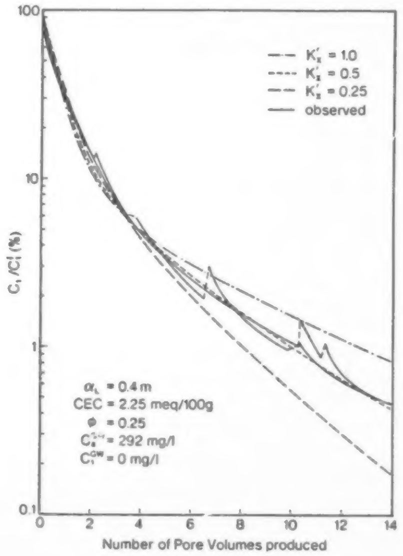

Figure 5. Ammonia production history compared to simulated history for various values of K'_x

Although it is not apparent from the figures, the "goodness of fit" at low concentrations is largely determined by the product (CEC•K'_x), rather than by CEC and K'_x separately. The value of the product can be determined with considerable precision, but, in the tests described here, the individual parameters are much less well defined. This difficulty can be overcome either by injecting higher concentrations of ammonium (Drever and McKee, 1980) or by injecting larger volumes. An estimate of the volume necessary can be made on the basis of laboratory measurements of adsorption properties and trial simulations.

Figure 6 shows the best match with observed data when a longitudinal dispersivity of 0.6 m is assumed. The best match is obtained with a CEC of 2.25 meq/100 and a K_x' of 0.25. The match in Figure 6 is slightly better for the first half pore volume than that in Figures 4 and 5. This illustrates the importance of estimating the dispersivity at the proper scale length before attempting to estimate adsorption parameters. Production history of total anions from the same push pull-test automatically provides an appropriate estimate of dispersivity.

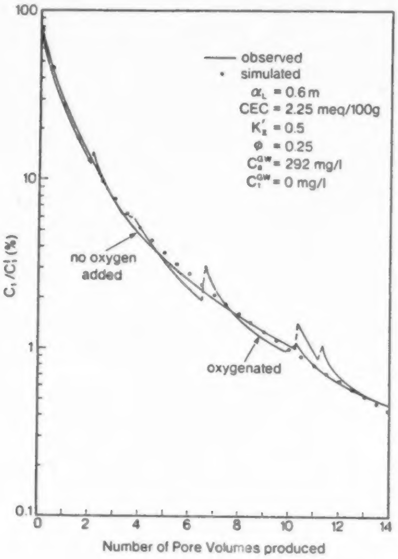

Figure 6. Ammonia production history compared to simulated history (longitudinal dispersivity)

CONCLUSIONS

1. One boundary condition used in previous simulations of the push-pull test is in error. The appropriate boundary condition is presented and its importance is demonstrated.
2. Dispersivity can be estimated from the production history of total anions or a non-adsorbing tracer.
3. In order to estimate adsorption parameters, dispersivity must be measured at the appropriate scale length.
4. Laboratory experiments are necessary to define the form of the adsorption equation, and to design the push-pull test.
5. If the push pull test is properly designed, individual adsorption parameters can be estimated with good precision.

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IDENTIFICATION OF SUBSURFACE BRINES USING STATISTICAL TECHNIQUE

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ABSTRACT

Statistical techniques have been successfully used to sort out the hydrogeologic process-response relationships from commonly collected groundwater quality data. The purpose of this study is to demonstrate the usefulness of the principal components analysis, a multivariate statistical technique, as a tool for mapping areas of distinct chemical features. The chemical analysis data of fifty-four groundwater samples have been used. The locations of the groundwater samples are distributed over an area of about 500 sq. km. in the Gangetic plain. Three components which represent different chemical processes have been identified, and their relative areal impacts have been determined. These components are, 1) localized concentration of chloride and T.D.S. due to scarce precipitation, high rate of evapotranspiration, and convergence of the groundwater flow; 2) dissolution and ion exchange in the semipermeable layer that overlies portions of the aquifer; and 3) regional dissolution of carbonaceous formation. The scores of principal components have been used to identify the saline water areas, and to distinguish the saline and non-saline water samples. A conceptual model has been proposed to represent the physical system.

INTRODUCTION

The rising saline and brackish water table has been causing alarm in the agricultural circles of Haryana. The present area of study in Gurgoan district of Haryana is part of this saline tract where pockets of high salinity have been identified. During the last couple of decades the attention of the local population and the State Government have been diverted towards the feasibility of reviewing the salt industry in the area and possible utilization of saline water coupled with reclamation of water-logged and saline land in the area. Therefore it is required to find the possible causes of brine formation and their areal extent in the area. The Principal Component Analysis is a multivariate statistical technique which has been used to map the areal extent of brine areas, to identify the possible modes of mixing of groundwater and to separate out the chemically distinct water masses.

The study area is a part of the Gangetic alluvial plain located between latitudes 28°, 23'N and 28°, 32'N and longitudes 76°, 42'E and 77°, 8'E, covering an area of about 500 sq. km. in Gurgoan district of Haryana State, India (Fig. 1).

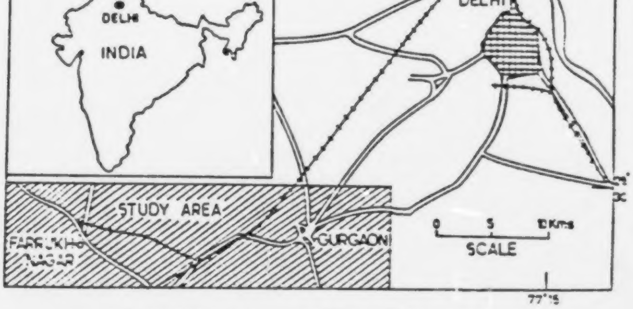

FIG.1. LOCATION OF THE STUDY AREA

HYDROGEOLOGIC SETTING

The area comprises almost flat plains interrupted at places by isolated tracts of sand dunes. The small outcrop of quartzite belonging to Aravalli super group is found in the eastern margin of the area. The alluvium in the flat plains in made of sandy clay, clay, silt, and Kankar (impure $CaCo_3$). The water bearing formations are composed of low permeability, semiconsolidated sands of varying grain size often interbedded with clay and Kankar beds. Ground water occurs generally under water table conditions. Subartesian conditions are also seen at places because of the occurence of thick clay beds at depths. The perched water table exists in sand dunes located near to the brine areas. The major acquifer is encountered below 10-20 metre depth from surface. The depth to water level varies from about 2-16 m below ground and in the central part of the area shallow water table conditions prevail leading to temporary water logging problems. The flow of groundwater generally follows the topography which is sloping toward the central part of the study area. The hydraulic gradient varies from about 1.5 to 4.0 m per km. Recharge to ground water takes place mainly through precipitation and partly from irrigation return flows.

THEORY AND PROCEDURE

The Principal Component Analysis (PCA), a multivariate statistical technique has been successfully used to sort out the geohydrochemical process-response relationships from commonly collected ground water quality data. Similar techniques have been widely used by Dawdy and Feth (1967), Lawrence and Upchurch (1976), Mathew and Dalton (1978), and Lawrence et al. (1982). For more details of the technique one may refer to Anderson (1958), and Morrison (1964).

In the present study R-mode principal component analysis has been used to analyze the original data matrix of ground water chemical quality. Since the component scores are calculated for each sample and they reflect the importance of a given component at that sample site, one can contour the factor scores for each component and evaluate the areal importance of the chemical process represented by that component. Dalton and Upchurch (1978) have shown that factor scores can be related to the intensity of the chemical process described by each factor. Extreme negative numbers (less than -1.0) reflects areas essentially unaffected by the process and the positive scores (greater than $+1.0$) reflect areas most affected. Near zero scores approximate areas affected to an "average" degree by the chemical process under study.

RESULTS AND DISCUSSIONS

The final component of original data matrix revealed three chemically distinct and mutually exclusive water masses. Total of 94.93 percent of the total variability has been accounted for, by the three principal components.

The first principal component is almost equally weighted on the positive direction of variable axes K^+, Ca^{++}, Mg^{++}, Na^+, SO_4^{--}, cl^-, TH, EC and TDS. This assembly of constituents is mainly derived from the leaching of the soils and aquifer material and partly from the impact of human activities like increased use of potassium fertilizer in the agriculture. Therefore this component is lithologically controlled. Fig. 2(A) shows the areal distribution of the first component scores. From the figure it is seen that there are three district areas characterized by high scores (greater than $+1.0$) with a discernible pattern. These areas coincide with the areas of brine water as indicated by conventional hydrochemical mapping (Khabya 1980). These are also characterized by natural ground water depressions, shallow water tables and high rate of evapotranspiration. The areas with scores between zero to 1.0 indicate the areas marginally affected by salinity. On the other, the rest of the area is characterized by negative scores interpreted as areas unaffected by dissolution and chemical process. These areas are seen to coincide with the ground water flow domain and recharge areas.

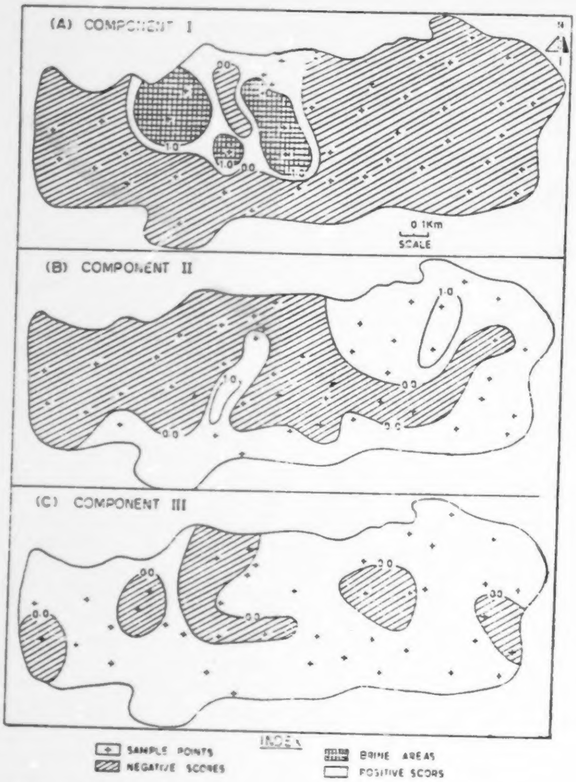

FIG. 2 AREAL DISTRIBUTION OF PRINCIPAL COMPONENT SCORES.

The second principal component which accounts for 10.12 percent of the total variance is mainly loaded on HCO_3^- (0.99). This constituent has no significant lithologic source in the area and therefore the only alternate source of HCO_3^- might have been the carbon dioxide in the root zone and zone of aeration which reacts with the percolating ground water and contribute HCO_3^- to ground water. Fig. 2(B) shows the areal distribution of the second component scores. From the figure it is seen that, but for two small areas where the scores are greater than one, the whole of the area is covered by near zero positive and near zero negative scores. This shows that the area is uniformly affected to an average degree by this constituent. However, the areas of positive scores are correlated with the areas of deep water levels where the percolating water has a greater chance to react with the CO_2 of the medium for a longer time to yield more HCO_3^- as compared to the shallow water table areas represented by negative scores.

The third principal component which accounts 6.19 percent of the total variance is mainly loaded on TH, Ca^{++} and Mg^{++}. The total hardness is influenced by Ca^{++} and Mg^{++} and these in turn are lithologically controlled assembly of constituents. Fig. 2(C) shows the areal distribution of this component scores. From the figure it is seen that the areas of brine pockets and saline water are represented by negative scores. This may be interpreted as due to the existence of Ca and Mg ions in the form of their respective salts and sulphates. The geohydrochemical studies in the area have also indicated that these salts and sulphates are dominantly found in saline and brine water areas. The areas of wide spread positive scores are the areas where Ca and Mg exists mostly in the form of independent ions.

The graphical plots of the scores of principal components is shown in Fig. 3. A, B, and C. From the figures it is seen that the first principal component can be successfully used as a guide to discriminate fresh and brine water samples and separate out the respective sample clusters.

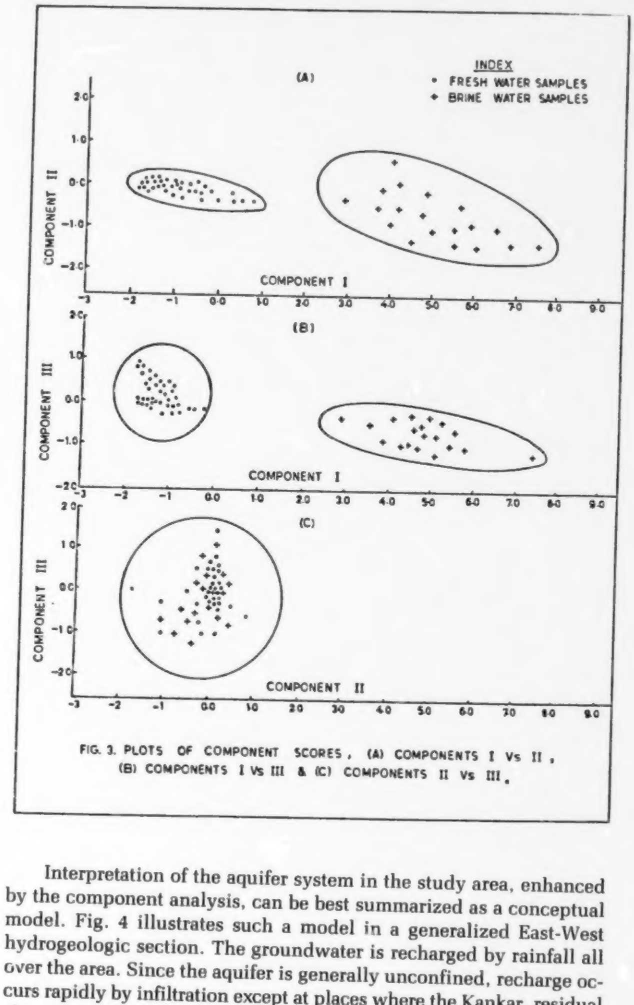

FIG. 3. PLOTS OF COMPONENT SCORES, (A) COMPONENTS I Vs II, (B) COMPONENTS I Vs III & (C) COMPONENTS II Vs III.

Interpretation of the aquifer system in the study area, enhanced by the component analysis, can be best summarized as a conceptual model. Fig. 4 illustrates such a model in a generalized East-West hydrogeologic section. The groundwater is recharged by rainfall all over the area. Since the aquifer is generally unconfined, recharge occurs rapidly by infiltration except at places where the Kankar, residual clay, and other Carbonaceous beds crop up near the surface. This is represented by component II water mass. As the percolating water moves through the aquifer Ca^{++} and Mg^{++} are released along with other constituents and this is represented by component III water mass. The moving water mass further gets mineralized as it travels toward the point of convergence where the stagnation of ground water and high rate of evapotranspiration because of shallow water table conditions enhances the concentration of salts in the groundwater. This is represented by component I water mass at brine water areas.

CONCLUSIONS

The areal mapping of each principal component scores has a significant role in explaining the variability of each constituents in the ground water. Plots of the scores of component I and III clearly

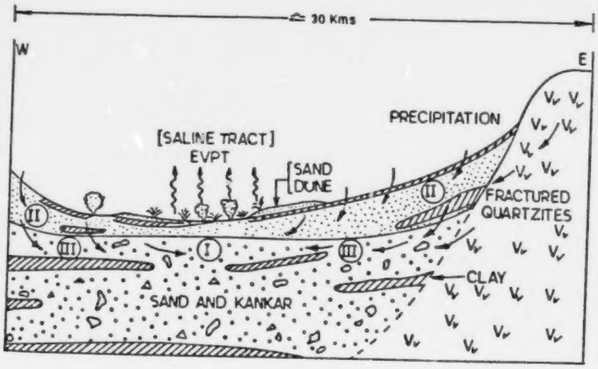

FIG. 4. GENERALISED HYDROGEOLOGIC SECTION OF THE STUDY AREA. ARROWS INDICATE MOVEMENT OF WATER. NOTE THAT COMPONENT II AND III WATERS MIX WITH COMPONENT I NEAR SALINE TRACT.

demarcate the brine pockets and saline water areas. The graphical plots of principal components can be succesfully used to sort out the saline and fresh water sample clusters. Water masses of distinct chemical features can be identified with their significance on the geological factors in the area. In the present study the technique has enhanced the building up of a conceptual model to explain the causes of the presence of brine water pockets in the area. This includes the confirmation that the brine water pockets in the area are not related to the connet water mixing or sea water enchroachment but their presence is mainly due to the high mineralization of ground water which is influenced by the geomorphologic feature, the subsurface geology, the direction of ground water movement, the stagnation of ground water, scarce precipitation and high rate of evapotranspiration due to extreme dry conditions.

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NEW METHODOLOGY FOR ASSESSING MUTAGENICITY OF WATER AND WATER RELATED SEDIMENTS

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ABSTRACT

Methodology not included in the EPA list, "Ambient Water Quality Criteria", is available for the rapid and cost-efficient assay of mutagens and physiologically detrimental agents which occur in waters, water related sediments and sludges. Both mutational and physiological effects resulting from such agents may be investigated simultaneously in the plant *Tradescantia*. There are three tests which involve separate end points: (1) the stamen hair test assesses somatic mutations at a single locus; (2) the micronucleus test is a measure of a germinal mutation caused by chromosome breakage or meiotic disturbances in pollen mother cells; and (3) variable fluorescence is a measure of perturbations in the elctron transport system of photosynthesis. All three tests are suitable for both short term and chronic exposures and for both field and laboratory studies.

INTRODUCTION

Water and the various kinds of sediments associated with water can be sources of mutagens and other toxic substances. Methodology not included on the EPA list, "Ambient Water Quality Criteria", is available for the rapid and cost-efficient assay of both mutagenic and physiologically detrimental effects simultaneously in the same organism, the plant *Tradescantia* (Spiderwort). There are three tests which involve separate biological end points: (1) the stamen hair test, which measures somatic mutations at a single locus; (2) the micronucleus test, which measures mutations as cytogenetic changes caused by chromosome breakage and/or the abnormal behavior of meiotic chromosomes in pollen mother cells; and (3) perturbations in the electron transport system of photosynthesis which may occur after exposure to toxic chemicals.

Tradescantia can be used for both short term exposures of minutes and hours and long term exposures of days and weeks to months, both on site under real-world conditions and in the laboratory.

DESCRIPTION OF THE TRADESCANTIA BIOASSAY SYSTEM

The three *Tradescantia* tests differ in their sensitivity and one or more of these tests may recognize physiologically hazardous or mutagenic agents that might go unregistered in the others. The use of the combined tests shold also permit accurate monitoring over a wide range of concentrations of toxic substances.

Tradescantia is particularly useful because of its versatility. Either cuttings or entire rooted plants may be exposed to gaseous agents in air or liquids, or grown in contaminated soils, grown hydroponically in, or watered with aqueous solutions of pollutants. Unrooted cuttings may be exposed for periods of minutes and hours, or up to 3-4 weeks, and rooted plants may be exposed for months if provision is made for suitable light and temperature conditions.

STAMEN HAIR TEST

Tradescantia has been used for radiobiological cytogenetic studies for over forty years. However, in the mid 1960's it was found that its array of long filmentous chains of contiguous, single cells growing from the stamens (stamen hairs) presented a plant structure which could be used as a sensitive and cost efficient test of chemical mutagens (Underbrink et al., 1973).

The average number of stamen hairs per flower, the denominator of mutation frequency, is routinely determined at the beginning of the scoring period. A total of 36 stamens from six randomly picked flowers are counted for each experiment. The average number of stamen hairs per flower ranges between 300-400. Each inflorescence (flower cluster) produces about 18-20 flowers; one blooms about every other day and the mutations appear as a phenotypic color change from the dominant blue to the recessive pink in cells in the stamen hairs of flowers of heterozygous clones. The mutation frequency is expressed as the number of mutant events per thousand stamen hairs.

In short term experiments scoring of stamen hairs for pink mutant events usually begins 5 to 7 days after treatment and continues daily until approximately 15 days after treatment, or until the number of mutations declines from any evident peak. The time from treatment to scoring constitutes time for development of buds from sensitive stages at which they are exposed to maturity when they exhibit the mutation events in the stamen hairs. If the plants are allowed to remain in a contaminated area for long periods of time, the scoring is done daily until the mutation frequency reaches a stable plateau or as long as the experiment dictates.

The sample size can be pre-determined and depends on the anticipated strength of the mutagen and percent standard error deemed acceptable (Underbrink et al., 1973; Underbrink and Sparrow, 1974). Mutagenicity studies using this test have been carried out routinely *in situ* in the field and in the laboratory with agents either in the gaseous or liquid state (Lower et al., 1978; 1983 a, 1983 b, 1984; Nauman et al., 1979; Schairer et al., 1979).

The following example illustrates the elevated stamen hair frequencies in *Tradescantia* [(frequency ± S.E.) x 10^{-3}] during five months of growing in sediment from a drinking water reservoir.

Sampling Period	Control	Sediment	P of Two Tailed Normal Approx. to Binomial
9/9-11/19	3.2 ± 0.3	5.6 ± 0.3	0.005
11/20-12/3	2.2 ± 0.1	4.2 ± 0.2	0.005
12/4-12/17	2.8 ± 0.2	3.6 ± 0.2	0.05
12/18-1/7	2.1 ± 0.1	3.3 ± 0.1	0.005
1/8-2/5	2.5 ± 0.3	3.1 ± 0.2	0.05

MICRONUCLEUS TEST

The micronucleus test of *Tradescantia* was developed in 1976 and is 6 to 8 times more sensitive than the stamen hair test (Ma, 1983). The mutagenic end point is the induction of chromosome breaks or lagging chromosomes which appear as micronuclei and are scored during the tetrad stage of meiosis in pollen development. After acetocarmine staining, the micronuclei appear as small dark red bodies in the pink cytoplasm and are easily distinguished from the much larger, dark red nucleus.

The preparation of inflorescences for scoring of micronuclei involves the following: After termination of the treatment period, cuttings are placed in aerated 1/2 strength Hoagland's nutrient solution in a controlled-environment chamber under a light regimen of 16 hrs light/8 hrs dark for 24-32 hours, which is the time necessary for the chromosomes damaged during early prophase of meiosis to progress to the tetrad stage of pollen formation (Ma, 1983). Flower buds are then fixed in ethanolacetic acid (3:1 ratio) for 4 to 30 hours, and transferred to 70 percent ethanol for storage.

For scoring, individual flower buds are removed from the inflorescences which have been stored in alcohol and the buds likely to contain the tetrad stage cells are selected based on bud size and position on the inflorescence. The anthers are dissected out of the bud, macerated, and stained with acetocarmine. Tetrads are scored at 400 X magnification. Approximately 300 tetrads are scored from each bud, and from 5 to 10 buds are scored for each experimental and control point.

The micronucleus test has been used as a method of estimating mutagenesis resulting from chromosome breakage in investigations of the mutagenic effects of a wide variety of environmental pollutants in water reservoirs, parking garages, truck stops, diesel exhaust, sewage sludge, cooling tower water, etc. (Clevenger et al., 1983; Ma, 1983; Ma et al., 1983).

An example of the application of the micronucleus test is illustrated by the frequency of micronuclei per 100 tetrads [average ± S.E. (n)] in cuttings of *Tradescantia* exposed for 8 hr to sewage sludge/water mixtures from sewage treatment plants of five Missouri communities. The control value of *Tradescantia* in water for all five sludges is 3.0 ± 0.8 (5).

Sewage Treatment Plant	25% Sludge	50% Sludge	P of Regression (b)
1	8.9 ± 1.8 (5)	32.0 ± 6.4 (4)	0.001
2	14.0 ± 1.9 (5)	15.0 ± 3.2 (5)	0.005
3	8.3 ± 1.5 (5)	13.5 ± 3.9 (5)	0.005
4	4.1 ± 0.3 (5)	11.5 ± 3.3 (5)	0.01
5	3.6 ± 0.4 (5)	7.6 ± 1.3 (5)	0.005

Another example is drawn from exposure of *Tradescantia* cuttings placed in the water from a cooling tower for 24 hours.

Control	Cooling Tower Water	P of One Tailed Wilcoxon Rank Sum Test
2.05 ± 0.40 (11)	5.27 ± 1.74 (11)	0.05

PERTURBATIONS OF THE ELECTRON TRANSPORT OF PHOTOSYNTHESIS

Room temperature chlorophyll fluorescence *in vivo* is a measure of oxidation-reduction state of the photosystem II primary acceptor (Q). Segments of leaves which are illuminated with a specific wavelength of light will fluoresce a range of wavelengths of light in response. Rapid changes in the yield of chlorophyll fluorescence occur within the first 15-30 sec. of illumination in all photosynthetic plants (Kautsky effect). This chlorophyll fluorescence induction can be used as a sensitive indicator of photosynthetic energy conversion and has been important in the characterization of photosynthetic reaction mechanisms.

The fluorescence induction curve (a plot of fluorescence against time for the period immediately following onset of illumination) is modified by many factors which affect photosynthesis. Present understanding of the various fluorescence transients allows the fluorescence induction curve to be used as an immediate and reliable test of photosynthetic activity. Variable fluorescence yield can be increased if electron transport is stimulated, or decreased if electron transport is inhibited depending upon where a given chemical produces a lesion in the complex chain of biochemical events prior to and including the photolysis of water in the Hill reaction through the reduction of NADPH.

Perturbations in electron flow are measured with a plant fluorometer, a portable AC/DC operated unit suitable for measurements in the field as well as the laboratory. It is connected to an AC/DC strip chart recorder. At the end of an exposure or treatment, samples of leaf material are collected and placed in plastic bags with moist cotton and dark-adapted for at least 15 minutes. A 2 cm segment of leaf is placed in a leaf holder. The fluorometer probe is inserted on top of the leaf segment, the dark adapted leaf segment is illuminated at 670 nm and simultaneous fluorescence at wavelengths greater than 710 nm is detected and recorded on the strip chart over 10 or more seconds (Govindjee, 1975; Schreiber et al., 1978). For each data point at least 10 strip chart recordings are made from 10 samples of leaf material and measurements are averaged to determine percent increase or decrease in variable fluorescence.

Two different perturbations in the electron transport system are illustrated by exposure of *Tradescantia* for 48 hours in the same cooling tower water discussed above in the micronucleus test: a) denotes percent variable fluorescence, average ± S.E. (n); b) denotes size of electron pool, average ± S.E. (n).

Control	Cooling Tower Water	P of One Tailed Wilcoxon Rank Sum Test
a) 59.85 ± 1.52 (10)	49.78 ± 2.59 (10)	0.01
b) 36.65 ± 4.27 (10)	19.50 ± 2.66 (10)	0.002

CONCLUSION

The *Tradescantia* system offers in one organism three cost-efficient tests of different sensitivities that can be used in the laboratory and *in situ* in the field to test soil, water and air contaminants for periods of hours to months. The attributes of *Tradescantia* indicate it should be given serious consideration for use in problems related to ground waters.

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MINIMIZING PROBLEMS CAUSED BY UNEQUAL DEVELOPMENT OF BIOLOGICAL ACTIVITY WITHIN COLUMN MICROCOSMS USED TO PREDICT THE FATE OF POLLUTANTS IN SUBSURFACE MATERIALS

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ABSTRACT

Microcosms are useful tools to predict the fate of chemical substances in natural systems. They can reveal the potential for occurrence of a particular process in the natural system of interest, and under appropriate circumstances can generate data on the kinetics of the process that can be used to model the real system.

In order to generate data that could be used for projections of kinetics, we constructed a microcosm that was as faithful as possible to the subsurface environment. Authentic subsurface material was collected in a way that avoided microbial contamination, then packed into sterile Teflon and glass columns. The material was exposed under aerobic conditions to concentrations of phenol; 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol in the range of 10-20 μg/liter. The chemicals were dissolved in sterilized ground water from the same layer of sand used to construct the microcosms. The flow rate in the columns was slow, about 2 cm per day, to simulate ground water flow.

After two months, a zone of intense biological activity developed at the head of the columns. This rendered the microcosms useless for any sort of kinetic analysis because it was impossible to determine the width of the active zone, and thus the residence time of the pollutants in that zone.

To minimize these problems, new microcosms were constructed, and the solution of chemicals was forced through them as rapidly as possible until the organic chemicals broke through in the column effluent. Then flow through the microcosms was stopped, except for the minimum volume needed for chemical analysis. Upon subsequent incubation, all the material in the columns experienced the same concentration of the pollutants, and the columns as a whole responded to the effects of the pollutants.

OBJECTIVE

This study uses column microcosms to characterize the transport, fate and kinetics of selected trace organic pollutants under aerobic conditions in the saturated subsurface. Subobjectives include advancing column microcosm technology by improving the sampling and associated analytical methods and applying the technology to (1) identify compounds that are subject to biodegradation, (2) examine environmental factors that influence microbial metabolism of organic pollutants, and (3) estimate the rates of pollutant transport in ground water. This paper reports on experiments with column microcosms operated under aerobic conditions. Column microcosms to study anaerobic processes are also being developed.

EXPERIMENTAL METHODS

Aquifer material for the column microcosms was obtained using the aseptic procedures developed by Dunlap, et al.(1977) and modified by Wilson, et al. (1981). Cores of saturated subsurface material (0.02% organic carbon content) were obtained that were uncontaminated by surface microorganisms. The site at which the cores were collected was sandy alluvium with no evidence of previous pollution by synthetic organics. The depth to the saturated zone was about 6 meters. The ground water had a temperature of 19°C with a dissolved oxygen content of about 4 mg/l.

The configuration of the column microcosms is shown in Figure 1. Four columns were filled with aquifer material in the laboratory under an ultraviolet hood and maintained in the dark at 19°C in an environmental chamber. Dosing water was collected by a Teflon cased well from the same depth immediately adjacent to where the aquifer material was collected. The water was filter sterilized under nitrogen pressure to prevent degassing. Pollutants were added to the water and applied to the columns with no headspace to prevent volatilization. Flow was maintained by the effluent pump at the rate of ground water movement in the field (2 cm/day) which corresponds to an effluent volume of about 38 mls/day.

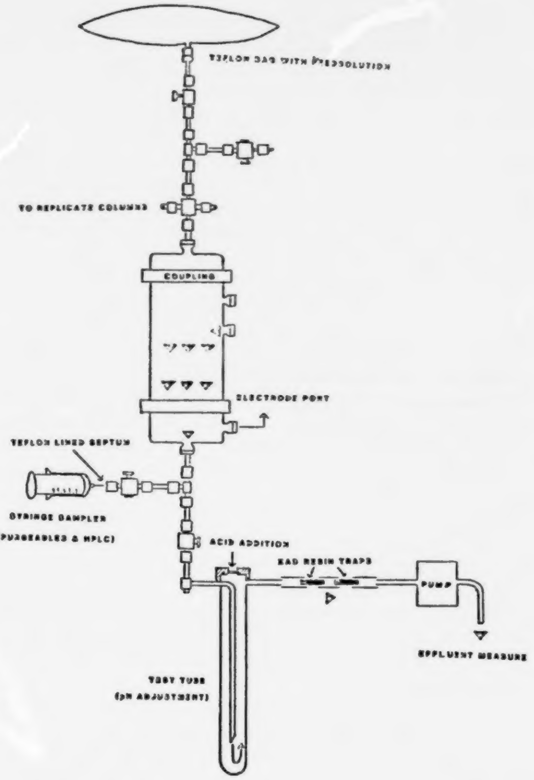


Figure 1: Dynamic Column Microcosm Design.

The entire system from influent through effluent sampling was composed of Teflon and glass. Samples were collected from the influent lines and column effluents through Teflon-lined septum by a sterile gastight syringe and by the use of a specially developed micro-XAD resin technique. A direct aqueous injection HPLC technique has also been developed for trace levels of phenolic pollutants (in the range of 10 μg/l). The involves on-line trace enrichment followed by chromatographic separation on a reverse phase column. Volatile pollutants were analyzed by convention purge and trap gas chromatography.

Of the four column microcosms three were initially fed dosed well water containing eleven priority pollutants each at the concentration between 10 and 20 μg/l. These include phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, chlorobenzene, 1,4-dichlorobene, 1,2,4-trichlorobenzene, 4-nitrophenol, toluene, tetrachloroethylene, and carbon tetrachloride. The fourth column was operated as a control fed with undosed well water. Five of the phenolic pollutants (phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol) were monitored.

RESULTS

After two months of operation approximately seven pore volumes of feed solution were applied to the columns. None of the monitored pollutants were detected in the column effluents. The influent concentration of the feed solution was then increased by a factor of three. After a similar application period the organic pollutants were still not detected in the column effluents. To determine the extent of biodegradation activity in the microcosms the feed solution was rapidly applied until the organic chemicals were detected in the column effluents at or near their influent concentration. Approximately three pore volumes of feed solution were applied to each column in 24 hours. The flow through the microcosms was then stopped. Samples were collected of the effluents (about 25 mls) periodically for two weeks.

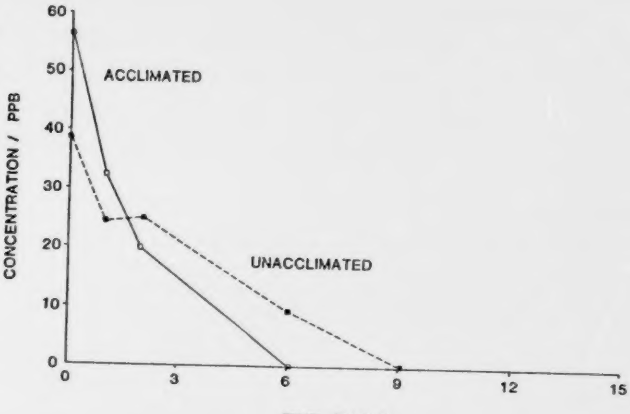
At the same time two new microcosms were constructed with unacclimated aquifer material. These columns were also hydraulically loaded with feed solution until the effluent concentration of the pollutants approximated the influent concentration. A comparison of the disappearance of 2-chlorophenol and 2,4,6-trichlorophenol in the effluent of an acclimated microcosm with an unacclimated microcosm is shown in Figure 2. In both cases, concentration of the substrates in the effluent of the acclimated column were reduced most rapidly. Slower reductions were observed with the unacclimated columns. This general pattern was also noted for the other compounds examined.

The disappearance of all five trace level pollutants was relatively rapid in terms of ground water movement under the experimental conditions. When the columns were initially operated as flowing systems it was not possible to determine the extent of the zone of biological activity. Thus it was not possible to determine the residence time of the pollutants in the biologically active zone and derive kinetic parameters for biotransformations.

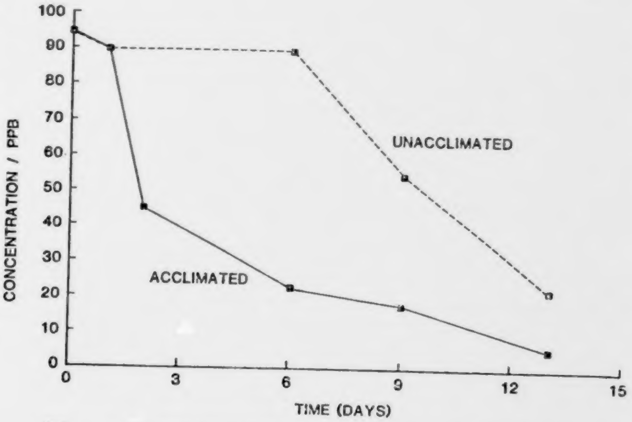
By comparing the disappearance of pollutants in previously exposed and unexposed microcosms the acclimation of subsurface microorganisms to xenobiotic pollutants can be observed when operated as batch systems. In the acclimated columns disappearance of the pollutants was most rapid with no evidence of a lag period. An indication of a brief lag period was observed in the unacclimated columns.

ACKNOWLEDGEMENTS

This study is part of a research project supported by the Environmental Protection Agency under cooperative agreement CR-811146-010. The assistance of several personnel from the U.S. EPA Robert S. Kerr Environmental Research Laboratory in aquifer material sample collection also contributed to this project.



(A) 2 - CHLOROPHENOL CONCENTRATION IN COLUMN EFFLUENTS



(B) 2, 4, 6-TRICHLOROPHENOL CONCENTRATION IN COLUMN EFFLUENTS

Figure 2: Disappearance of Pollutants from the Column Effluent of Microcosms

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QUANTIFYING GROUND-WATER STORAGE AND INTERACTION IN A MULTI-LAYERED ALLUVIAL AQUIFER

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ASBSTRACT

Comparisons are made between total penetration wells and those completed in selected layers of the Washita River alluvium near Anadarko, Oklahoma in order to determine the effects of layered lithology on aquifer yield. The hydraulic characteristics developed from analysis of core samples from individual sand and silt layers within the alluvium are used to estimate groundwater storage and movement within the alluvium.

Pumping tests of a nearby total penetration irrigation well and those from research test wells are compared in order to relate yield determined by analytical techniques to that of a producing well. Aquifer test results are presented for wells in specific layers. A unique relationship between the D_{50} grain size and the permeability within each layer is demonstrated which makes it feasible to use the laboratory test, rather than the more expensive pumping test to determine permeability.

The results of the multi-layered and homogeneous cases are compared using a map of transmissivity residuals which indicates areas of reduced storage within nearly 70,000 acres of aquifer during a 20 year period of simulated pumping in the Washita River alluvium.

INTRODUCTION

Increased use of ground-water supplies throughout the Plains States has created the need for better information on changes in ground water storage in fluvial deposits associated with irrigated agriculture. The long term pumpage of ground-water affects the farm management practices and economic development of such areas, particularly in areas of shallow alluvium of limited extent. The objectives of this study are 1) to relate changes in ground water storage to dewatering characteristics related to the lithology of a major river alluvium, and 2) to compare layered and homogeneous aquifer properties in terms of the storage and potential for transport of ground water and related chemicals or nutrients, under an intensely irrigated agricultural management scheme. The area selected for study is the alluvium along the Washita River between Anadarko and Alex, Oklahoma.

The Washita River alluvium, within the study area, overlies Permian age shale and sandstone deposits which serve as lateral and lower boundaries to the unconsolidated alluvial aquifer. Lithological data was originally obtained for a selected pump testing site and lithologic zones were characterized on the basis of grain size distribution analysis.

Subsequent parameter development for a digital model was based on the relationship found between those data and hydraulic properties, such as permeability (K_s), storage coefficient (S), specific yield (S_y) in water table conditions, and transmissivity (T) related to saturated thickness of zones within the alluvium.

AQUIFER TESTS

The Allenbaugh aquifer test site is located in T7N, R9W on the border of sections 8 and 9. This is near the eastern edge of central Caddo County, and approximately 4 miles east and 1.5 miles north of Anadarko, Oklahoma. The site lies within the Washita River basin between Anadarko and Alex, Oklahoma (Figure 1), and is situated in the first terrace of the Washita River alluvium.

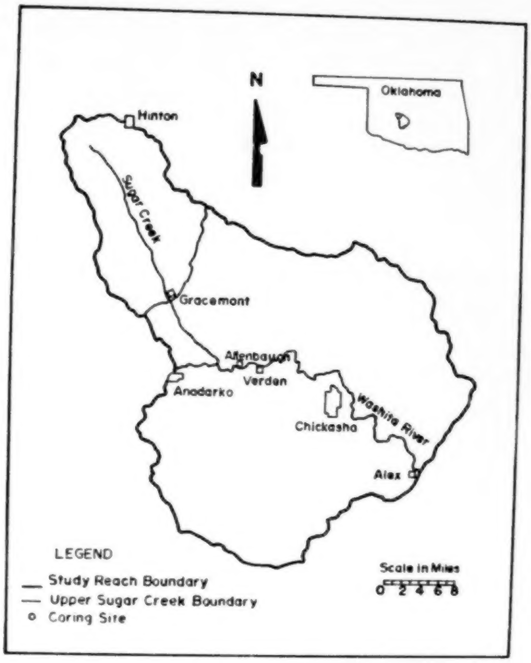

Fig.1 Location Map

For this study, four pumping wells were used, one well to test the total aquifer thickness and one well to test each of the three individual zones. Monitoring piezometers were established in two groups of three each, north and west of the pumping wells. Each group had one piezometer monitoring each of the zones. The total interval was monitored from an irrigation well 53 feet south of the total penetration test well which had perforations from 20-60 ft. deep.

PUMP TEST ANALYSIS

Six different graphical methods were used to analyze pumping test drawdown and recovery data, and calculate values for transmissivity, permeability and storativity. These methods include the Theis (Theis, 1935), Jacob Straight Line (Jacob, 1950), Hantush (Hantush, 1956), Hantush Inflection Point (Hantush, 1956), Prickett (Prickett, 1965), methods for drawdown analysis and Jacob (Jacob, 1950), method for analyzing recovery data.

RESULTS

Both drill cuttings and cores were used to help determine stratigraphic boundaries. Sediments were classified, on the basis of grain size, by analysis of drill cuttings and core samples, using a visual accumulation tube. The modal grain size and relative grain size sorting were determined on each sample. Grain size categories are given in Table 1. The median grain size (D_{50}), uniformity coefficient (U_c), and

Table 1. Grain size classification for drill samples from the Allenbaugh site.

Grain Size Catagory	Symbol	Size Range (mm)
Silt	S	.062
Very Fine Sand	VF	.062-.125
Fine Sand	F	.125-.250
Medium Sand	M	.250-.500
Coarse Sand	C	.500-1.000
Very Coarse Sand	VC	1.000-2.000

average coefficient of permeability (K) for each zone individually, and for the total saturated interval, are listed in Table 2.

Figure 2a shows a view of the Allenbaugh site and a north - south cross section is shown in Figure 2b. The terrace can be divided into three distinct lithologic intervals. The upper zone consists of very fine and fine, well sorted sand. Some interbedded clay lenses are also present. Most of this zone lies above the water table.

The middle zone is a heterogeneous mixture of medium, fine and very fine sand layers, often interbedded with clay. The middle zone is overlain by a thin clay aquitard 7.5-15 cm thick.

The bottom zone is composed primarily of coarse and medium sand, but also contains gravel, cobbles, fine and very fine sand. The unit is covered throughout the site by a layer containing clay and sandy clay ranging from 1.0 to 1.5 feet thick, which acts as an aquitard between the middle and bottom zones. The bottom zone rests directly upon impermeable Marlow shale which forms a lower hydraulic boundary to the system.

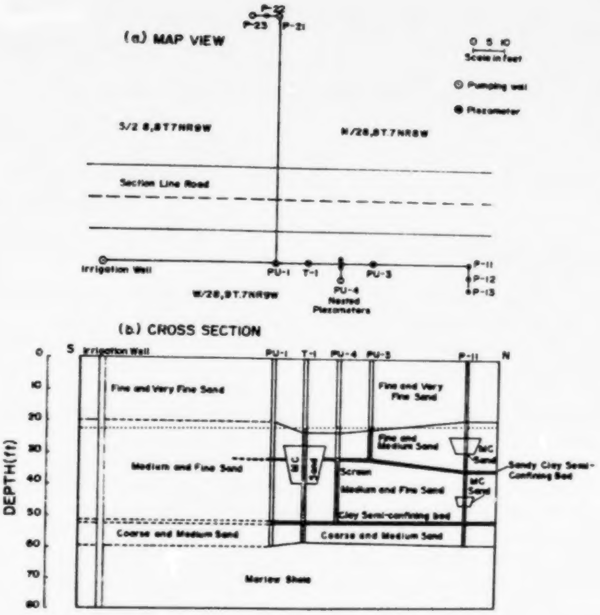

Fig.2 Cross-section and map view of Allenbaugh test site.

Aquifer test K vs the average D_{50} and U_c from the tested interval was plotted as shown in Figure 3. The uniformity coefficient (U_c) is equal to the grain size coarser than 60 percent of the sample divided by the grain size coarser than 10 percent of the sample. Curves of equal U_c were drawn for the data in Figure 3 by contouring the U_c values. For well sorted fine to very coarse sand, the U_c roughly parallel each other. The permeability values, obtained from the Hantush Curve, Hantush Inflection Point and Prickett methods were averaged together for each of the Allenbaugh aquifer tests.

Table 2. Average values of K, D_{50} and U_c within lithologic zones of the alluvium.

Well	Zone	Thickness (FT.)	D_{50} (AVG.)	U_c (AVG.)	METHOD OF ANALYSIS			
					Hantush (gpd/ft^2)	Hantush Straight Line (gpd/ft^2)	Prickett (gpd/ft^2)	Mean K (K vs D_{50} plot) (gpd/ft^2)
Pu-3	Upper	11.2	0.165	2.63	--	--	--	56*
Pu-4 (1st Test)	Middle	20.0	0.182	2.84	122	222	150	165
Pu-4 (2nd Test)	Middle	20.0	0.182	2.84	60	438	148	104
Pu-1	Bottom	7.0	0.535	2.49	2430	2135	1960	1365
T-1	Total	34.4	0.341	2.94	340	394	348	361

*Average of slug test methods used to calculat upper zone data

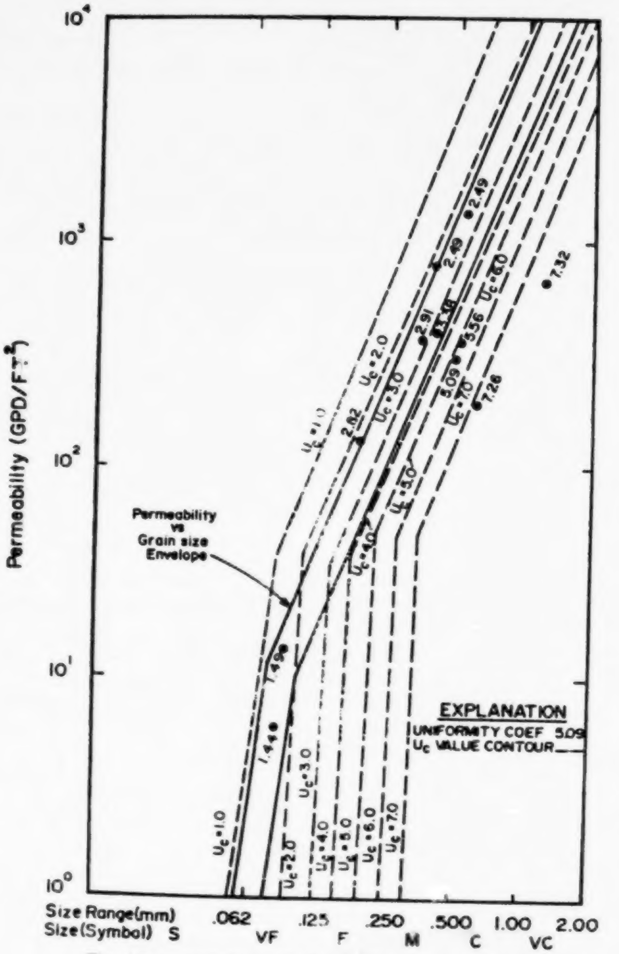

Fig.3 Permeability vs D_{50} Grain Size from Aquifer Analysis

DISCUSSION

The similarity between permeability vs grain size distribution plots and uniformity coefficient curves for aquifer test data suggests that the relationship between permeability, median grain size and uniformity coefficient represents the hydraulic characteristics of the subsurface material more than the technique used to measure permeability, and is applicable over a broad range of lithologic materials.

The boundaries for the permeability - median grain size envelope developed by Kent (Kent, et al., 1973), represents the most common degrees of sorting found for the various grain size classifications in the alluvial sites that were examined. The envelope boundaries do not follow a single uniformity coefficient curve, but roughly parallel all the curves. The U_c curves determined in the laboratory provide a practical means of estimating permeabilities, for a wide variety of unconsolidated sands, without conducting more expensive and time-consuming aquifer or permeameter tests.

APPLICATION

A finite difference model developed by Trescott, et al. (1976) which uses initial ground-water levels, surface discharge, and permeability as input parameters were used to model ground-water level and storage within the aquifer. The model output is a map of predicted ground water head elevations and an estimated volume of ground water in storage at the end of the specified time period.

Assignment of the coefficient of permeability was based on the grain size distribution-coefficient of permeability envelope shown in Figure 3. These data were contoured, digitized and used in the program.

A map of transmissivity residuals (layered-homogeneous) are used to compare the homogeneous and layered concepts for computer modeling of the Washita River alluvium as shown in Figure 4. This map shows the impact on the basin when pumping the recommended maximum annual yield of 70,000 acre feet/year (proportioned as 1.6 acre feet/acre/year). Also, the map indicates areas of higher transmissivities where high permeability sands dominate the lithology. The map in Figure 4 indicates a more conservative estimate of aquifer dewatering results when the homogeneous case is assumed. Thus, assuming the layered case when modeling alluvial systems should provide more realistic estimates of available water yield and storage depletion from irrigated lands.

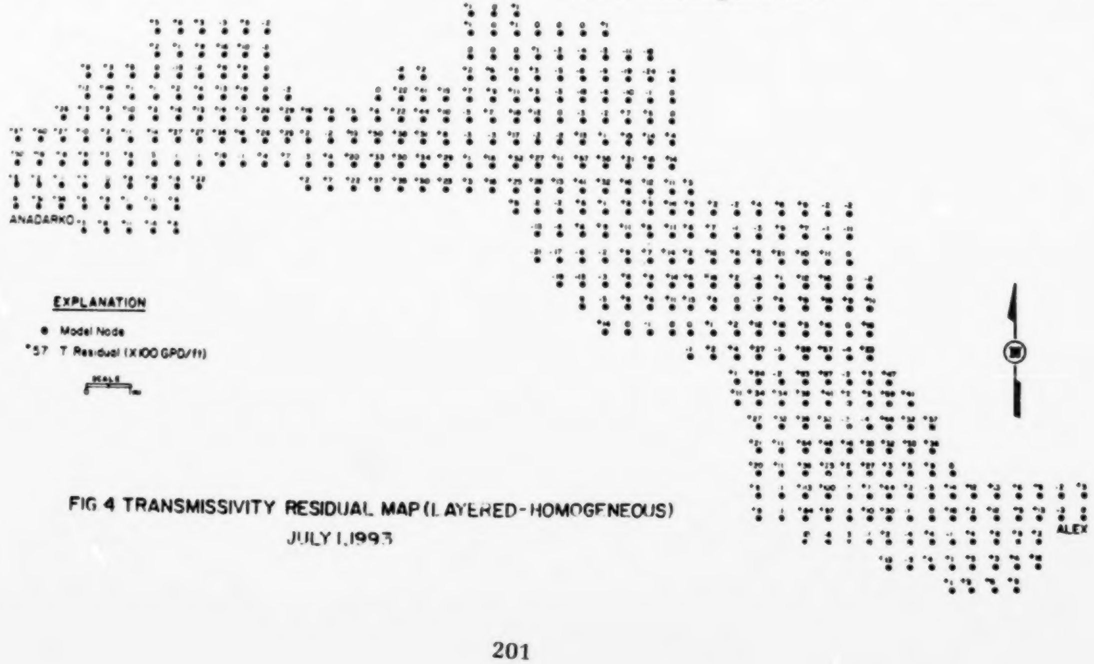

FIG 4 TRANSMISSIVITY RESIDUAL MAP (LAYERED-HOMOGENEOUS)
JULY 1, 1993

SUMMARY

Methods were developed to determine values of hydraulic properties for a layered alluvium. The data analysis provided an envelope based on the relationships found between permeability, uniformity coefficient and grain size.

The resultant envelope was used to develop data sets of subsurface hydraulic parameters to be used as inputs to a digital mathematical model. Finally, these generated input data were used to predict long term (20 year simulation period) aquifer dewatering patterns for a homogeneous alluvium compared with an alluvium containing hydraulically distinguishable lithologic zones.

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USE OF ELECTRICAL RESISTIVITY METHOD TO STUDY VERTICAL HYDROLOGIC BOUNDARIES IN WADI SUDR, SINAI PENINSULA, EGYPT

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ABSTRACT

The method of electrical resistivity sounding was applied to the Delta of Wadi Sudr in Sinai Peninsula to study, within the upper 25-35 m of Pliocene and Quatunary strata, the relation between the lithologic succession and the presence of both fresh and saline water bearing formations at different depths. Interpretation of the sounding curves indicates that the geoelectric succession in the area corresponds to hydrologic rather than lithologic boundaries. The results indicate that:

1. Four geoelectric layers are recognized which represent the soil zone, aeration zone, fresh water zone and sea water zone.
2. Depths of the boundaries between these zones are 1-2.5 m, 4-10.5 m and 21-27 m respectively from ground surface.
3. Resisitivities of the four geoelectric layers are 53-1000 ohm.m, 25-343 ohm.m, 18-120 ohm.m and 5-16 ohm.m respectively.

The results obtained show good agreement with the known geologic and hydrologic settings of the area and the method used is proved to be useful in locating vertical hydrologic successions. The results show also that water wells to be drilled in the future in the area should not exceed a depth of 25 m and that pumping rates and periods should be under accurate control as to the change in water quality due to over-pumping.

INTRODUCTION

The present study is mainly concerned with the geophysical investigation carried out in the Delta of Wadi Sudr using the method of electrical sounding. The main objectives were to reveal the configuration of the water bearing formation in the area including its depth, thickness and extension, to find the depth of sea water intrusion in relation to the fresh water-bearing formation and to specify the resistivities of the different rock types or key horizons extending from the surface to the saline water zone so that they might be followed out in similar areas along the western coast of the peninsula for locating subsurface hydrologic boundaries.

Location:

Wadi Sudr lies in West Central Sinai on the eastern coast of the Gulf of Suez as shown in Fig. 1. It is a fluvial plain extending between

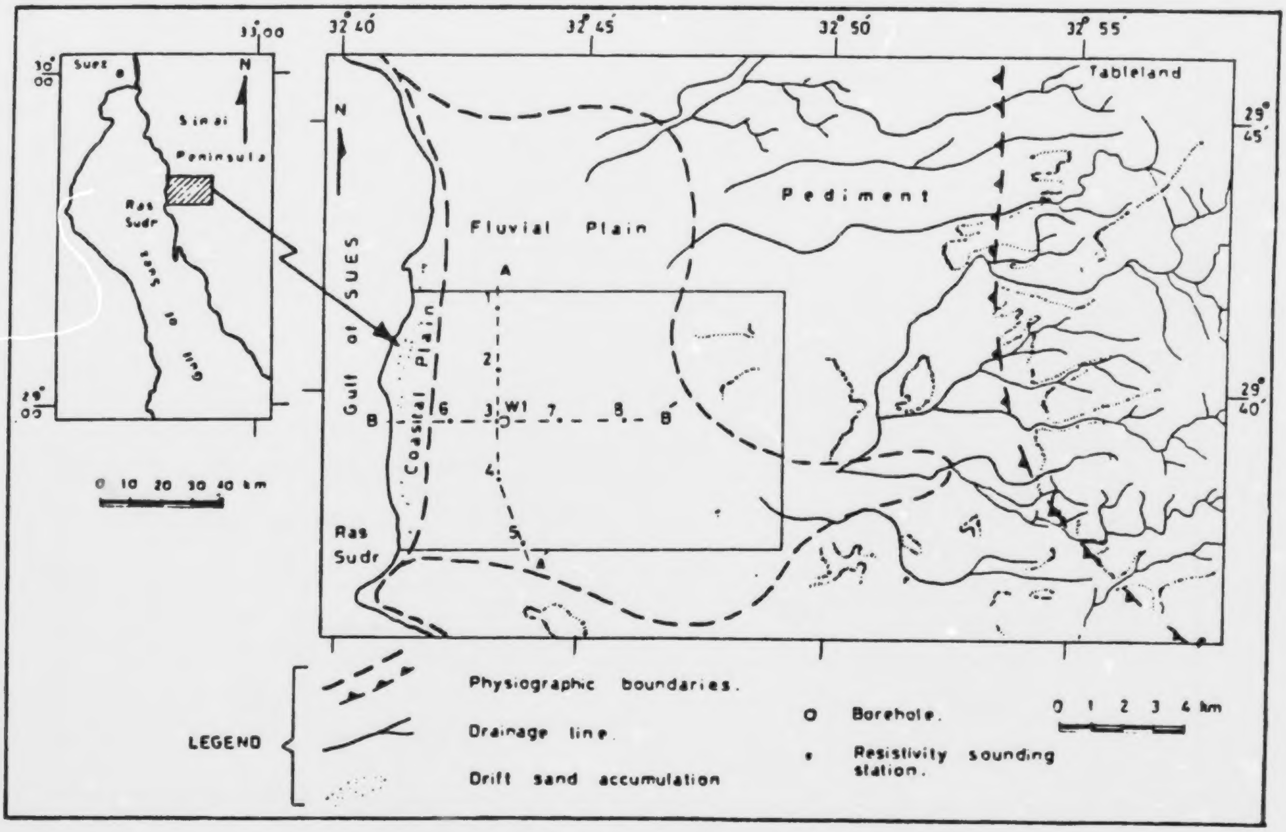

Fig.1 Location and physiographic map of the area .

Latitudes 29° 35N, 29° 45N and Longitudes 32° 40E, 32° 50E, bounded from the east by the Mountainous Plateau and from the west by the Gulf of Suez. The Delta of Wadi Sudr is a flat lying land with a length of 4-8 Km, width of about 5 Km, and an elevation of 22 to 27 m above sea level.

Geomorphologic, Geologic and Hydrologic Features:

Four main geomorphologic units are recognized in the area including Wadi Sudr which control topography, rainfall, flood tracks and ground water recharge. These units, shown in Fig. 1, are the Plateau Region, the Piedment Plain, the Flood Plain and the Coastal Plain. The Plateau Region has an average elevation of 600 meters and is covered by the Neogene calcareous rocks. It is dissected on its western slopes by several dry valleys. Such valleys become active in winter time and flood water is drained toward Wadi Sudr where it partly percolates to recharge the groundwater reservoir and is partly lost in the Gulf or by evaporation. The Piedment Plain lies right to the west of the Plateau Region and is covered by the Miocene marine deposits. The Fluvial Plain includes most of the delta and is covered by recent deposits in the form of loam, sand and alluvium in the downstream part of Wadi Sudr and coarse sand and gravel upstream. The Coastal Plain is a narrow belt running parallel to the Gulf coast and is covered by recent drift sands and small dunes close to the coast line. In the subsurface, previous regional studies as well as recent drilling indicate that Pliocene and Pleistocene sand, clay and gravel are present in the form of intercalated layers and lenses forming the shallow succession where groundwater is present under free condition and the aquifer is underlain either by sea water or clay layers.

The area receives an average rainfall of 50-70 millimeter per year on its eastern high-land part and only 20 millimeter per year on the delta part.

FIELD RESISTIVITY MEASUREMENTS

Resistivity measurements were made through 8 vertical electrical soundings arranged along two profiles as shown in Fig. 1. Profile A-A′ is 8 Km long and runs in the N-S direction. It includes soundings 1,2,3,4 and 5. Profile B-B′ is 7 Km long and runs E-W including soundings 6,3,7 and 8. The two profiles intersect at the location of sounding 3 at which borehole W1 is located. The Schlumberger electrode configuration was used in the field survey as it was proved to be helpful in getting rapid and reliable results in similar coastal area of Sinai Peninsula and the Western Desert. The maximal length of the current line ranged from 200 m to 350 m. Measurements ended always wherever it was difficult to measure accurately the potential difference Δv due to the effect of sea water intrusion into the area. Steel rods were used as current electrodes while non-polarized copper-copper sulphate electrodes were used for potential measurement at short spreadings. For long spreadings the non-polarized electrodes were replaced by copper rods. The measuring instrument used is the "Electronic Compansator 'SK-1' " which enables both the current and potential to be measured with good accuracy.

Field measurements started with sounding 3 where the lithologic log and water level are known so that correlation between geoelectric, lithologic and hydrologic successions could be made possible.

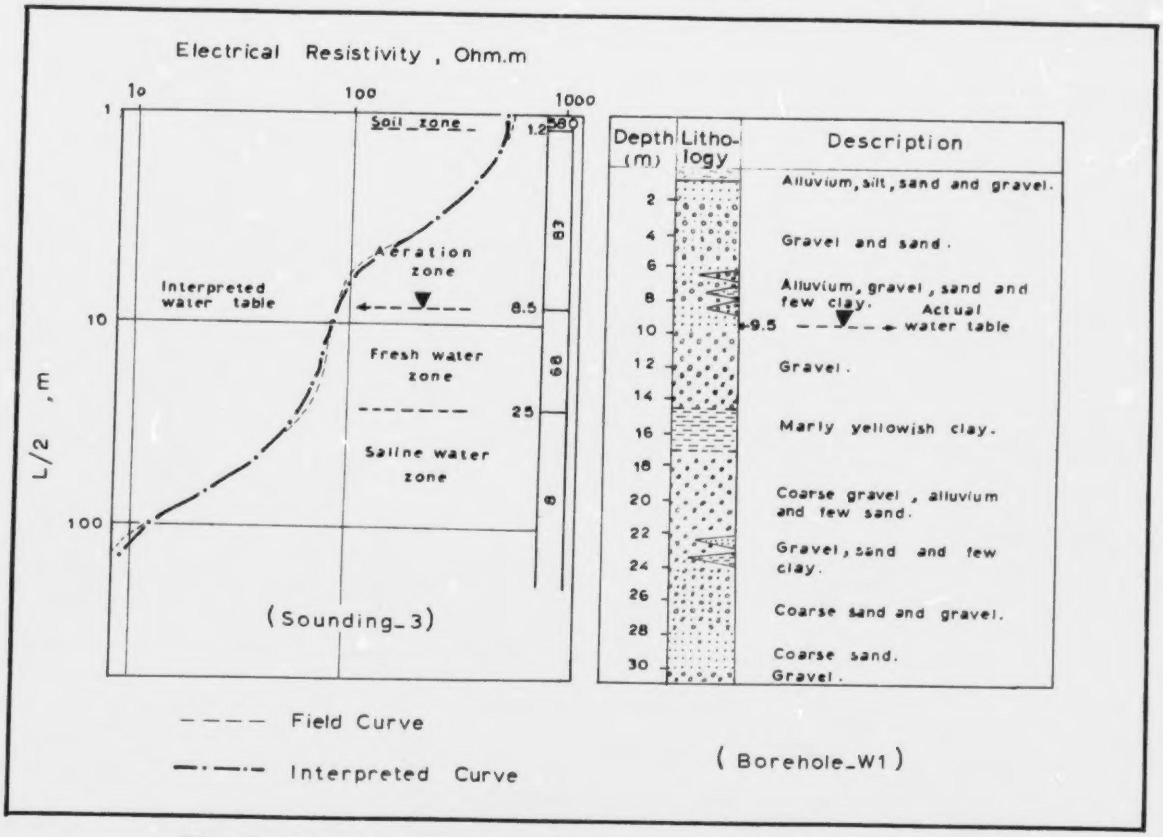

Fig. 2 Geoelectric section and lithology at the location of borehole W1.

The other soundings were then carried out along profile A-A′ and B-B′ respectively.

INTERPRETATION AND DISCUSSION OF THE RESISTIVITY DATA

Interpretation of the resistivity curves was carried out using Zohdy's "Computer Program for the Automatic Interpretation of Schlumberger Sounding Curves Over Horizontally Stratified Media, 1973". The section concluded from sounding 3 was first studied in relation to depth to water table and vertical distribution of the different rock units at borehold W1. Figure 2 shows the geoelectric section concluded for sounding 3 as well as lithology and water level at borehole W1, while Table 1 summarizes the results of interpretation and correlation at that point.

Table 1. Geoelectric, lithologic and hydrologic successions at sounding station 3.

Geoelectric layer	Depth to top m	Thickness m	Resistivity Ohm.m	Lithology	Hydrologic horizon
Surface	0	1.2	580	Alluvium, silt, sand and gravel	Soil Zone
2	1.3	7.3	83	Gravel,sand alluvium & few clay.	Aeration Zone
3	8.5	16.5	68	Alternating sand,gravel and clay	Fresh water zone
4	25	-	8	Coarse sand and gravel	Saline water zone

The first discontinuity on the sounding curve at depth of 1.2 m separates the surface layer which consists of course dry alluvium, silt, sand and gravel from the second layer consisting of gravel, sand and few clay. Field investigations showed that the second layer is more compact than the surface one and contains more soil moisture. This explains the drop in resistivity from 580 to 83 ohm.m. The first discontinuity is thus regarded to mark the boundary between the soil zone and the aeration zone.

The second discontinuity is observed at a depth of 8.5 m marking the top of the third geoelectric layer which consists of coarse sand and gravel with a thickness of 16.5 m. and is interrupted by a marly clay layer 2.5 m thick at the depth of 14.5 m. This layer represents the water bearing formation in the area where water level measurement in borehole W1 indicates that the water table is at a depth of 9.5 m which is very close to the interpreted depth. The marly clay layer is seen on the lithologic log to divide the water bearing formation into two horizons. No response, however, is detected for this layer on the sounding curve. On the other hand, analysis of the water samples indicates that the water E.C. is 5 millimhos/cm, that is 3200 p.p.m. total dissolved solids. It is then most likely that the effect of the entire section of the water bearing formation, including the clay layer saturated with water having that quality, masks the effect of the clay layer alone which would, otherwise, appear on the sounding curve as a separate resistivity low at the depth interval of 13.5-17 m. The resistivity of the water bearing formation is 68 ohm.m which is lower than that of the aeration zone as the later is considered to be relatively dry.

The last discontinuity is observed on the sounding curve at a depth of 25 m which is regarded to mark the fresh water-saline water interface taking in consideration the sharp drop in resistivity from 68 ohm.m to 8 ohm.m, the elevation of the sounding stations which is about 22 m and the fact that with overpumping in the area, water quality rapidly deteriorates.

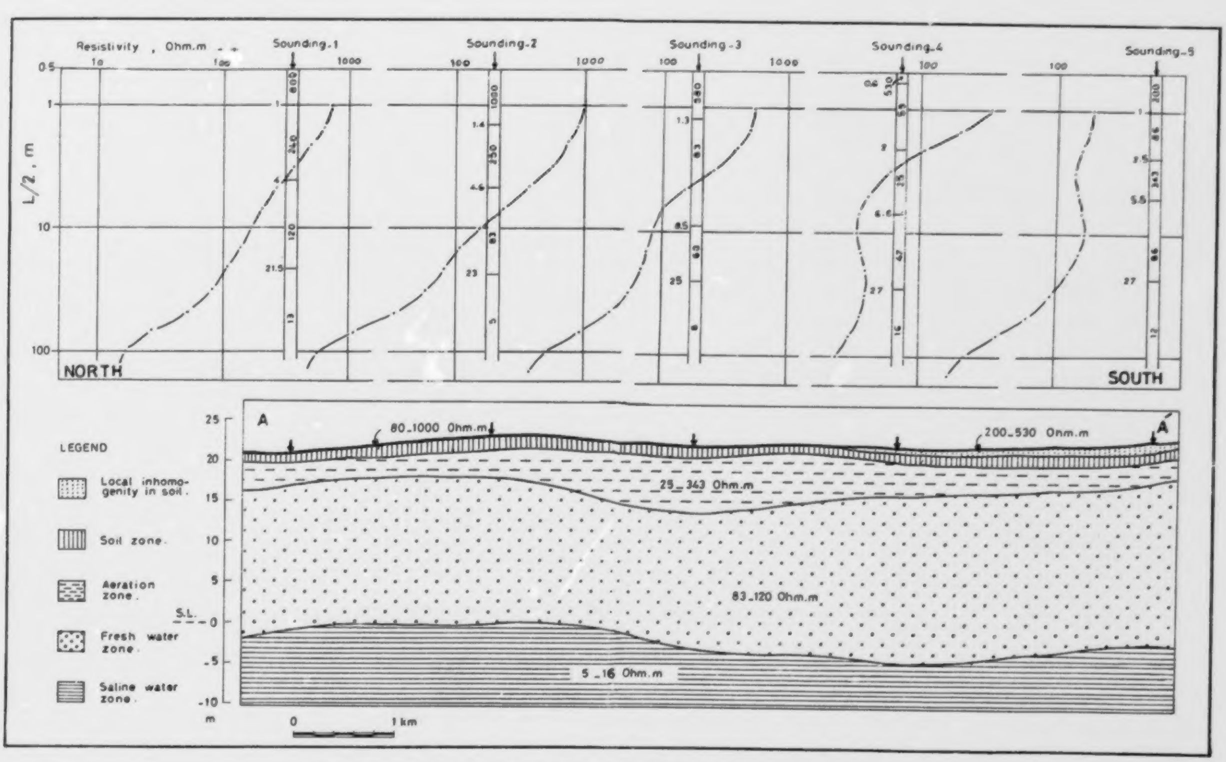

Fig.3 Geoelectric_hydrologic section along profile A_A

These 3 discontinuities are regarded to be due to hydrologic rather than lithologic boundaries. This is because the lithologic section of the area consists generally of alternating gravel, sand and clay with no sharp change from one type to another. Consequently, resistivity values would be mainly affected by the water content and water quality of the different rock horizons. This rends the fresh water-saline water interface, the water table and the boundary between the soil and aeration zones to be good markers on the sounding curves.

Guided with the above argument, interpretation of the other sounding curves was carried out from which it was possible to find that the geoelectric section in the area consists of either 4 layers as in soundings 1,2,3,7 and 8 or 5 layers as in sounding 4,5 and 6 as shown in Fig. 3 and 4. The fifth layer represents surface deposits of local extension overlying the main 4 - layer succession of the area. It consists of silty sand to sandy silt with resistivity varying from 80 to 530 ohm.m and is regarded as local inhomoginity in the surface layer. The 4-layer succession consists of the soil zone, aeration zone, fresh water zone and saline-water zone. Variation in depth, thickness and resistivity of each zone is illustrated by the two cross-sectional profiles of Fig. 3 and 4 and is summarized in Table 2.

Three important parameters related to the future development of the area can be figured out from Fig. 3 and 4 as well as table 2 which are the thickness of the soil cover, depth to water table and depth to the fresh water-saline water interface. The importance of these parameters lies in the fact that it is the first time to try detecting soil or water vertical boundaries through resistivity measurements in this particular part of Sinai Peninsula, furthermore they can be utilized in carrying out more detailed survey in the area or the adjacent coastal areas.

Table 2. Geoelectric and hydrologic succession in the Delta of Wadi Sudr.

Geoelectric layer	Depth to top, m	Thickness m	Resistivity ohm.m	Hydrologic horizon
Surface	0	1-2.5	50-1400	Soil zone
2	1-2.5	3-9.5	25-340	Aeration zone
3	4-10.5	12-20	18-120	Fresh water zone
4	21-27	-	5-16	Saline water zone

Taking the results of this work in consideration, it is recommended that water wells taping the free aquifer in the area should have a total depth of not more than 25 m and that the pumping rate and period of each well should be under control to avoid saline water encroachment in that coast area.

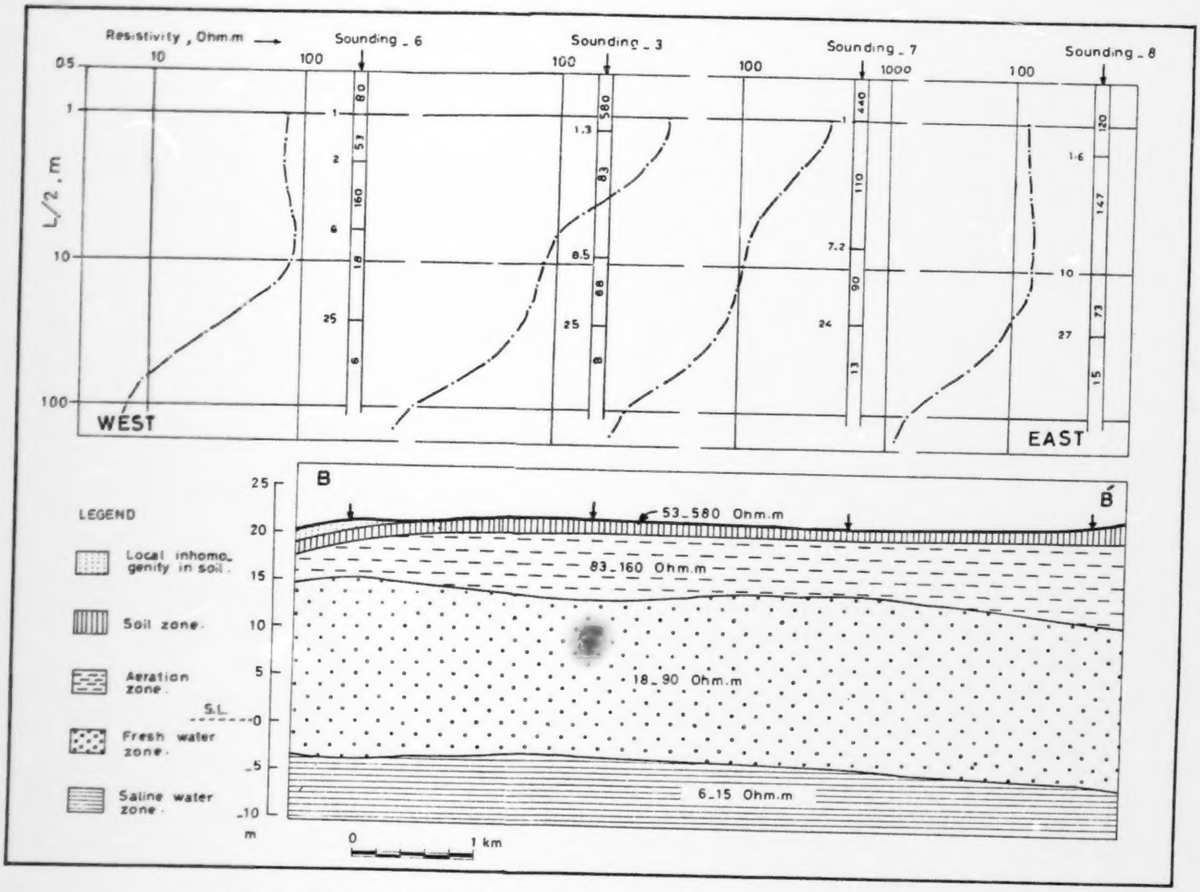

Fig. 4 Geoelectric _ hydrologic section along profile B_B́

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SIMPLIFIED GROUNDWATER SAMPLING TECHNIQUES AT LANDFILLS

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ABSTRACT

The Department of Water, Air and Waste Management (WAWM) for the State of Iowa established protocol for groundwater sample collection at landfills. A "non-protocol" collection technique was used at the Clinton County Area Solid Waste Agency (CCASWA), East Landfill Site, in Clinton, Iowa, to reduce labor costs. When three (3) successive semi-annual sample analyses exceeded the lead concentration standard at a single monitoring well for the municipal landfill, WAWM requested a comprehensive and costly site investigation. Subsequently, a reduced scope of investigation was negotiated between WAWM and CCASWA. WAWM agreed that, if the reduced scope investigation could prove (1) that non-protocol sampling was environmentally conservative, and (2) there was no tendency for increased lead concentration with respect to time, then the CCASWA could continue non-protocol sampling, so long as groundwater contamination levels were below the threshhold limits. A statistical analysis of the difference between the collection techniques indicated the non protocol technique is environmentally conservative compared to the protocol collection technique, with a 90% degree of confidence. Regression analysis of the laboratory tests of non-protocol-collected samples indicated there was no tendency for increased lead concentration with time.

BACKGROUND

To reduce operating costs for the Clinton County Area Solid Waste Agency's (CCASWA) East Site Municipal Landfill at Clinton, Iowa, groundwater sample collection from monitoring wells was shortened from the sample collection protocol established by the Department of Water, Air and Waste Management (WAWM) for the State of Iowa.

Briefly, WAWM protocol requires water withdrawal, then recovery in the monitoring well, before a sample is to be taken. The sample then is to be filtered on-site and preserved with nitric acid prior to transport to the laboratory for analysis. The shortened method of sample collection was simply to bail the monitoring well dry, wait approximately 2 to 3 hours, remove a sample, and transport it to the laboratory. The shortened or "non-protocol" sampling collection technique is estimated to require only one-third the amount of manpower compared to following the established protocol.

Verbal consent for non-protocol sample collection was given to CCASWA by WAWM. However, when three successive semi-annual samples from a single groundwater monitoring well showed that the lead concentration exceeded the established threshhold, WAWM requested a detailed study to identify the cause of the increased lead concentration. That study was estimated to cost over $10,000.

CCASWA contended that an overall trend of increasing lead concentrations had not been established and did not support the degree of concern exhibited by WAWM; and further, the non-protocol sample collection technique tended toward higher values. Based on these contentions, WAWM agreed to reduce the scope of the investigation to a statistical analysis of the trend of increasing lead content in the single groundwater monitoring well and a verification of the environmental conservatism associated with the non-protocol sample collection technique. If it could be shown that the non-protocol sampling method resulted in a predictably higher lead concentration (Hypothesis #1) and that there was no trend toward increasing lead concentration from the monitoring well (Hypothesis #2), WAWM would allow CCASWA to continue their non-protocol sample collection technique so long as contaminant levels did not exceed the established threshhold set for lead concentration in the groundwater.

METHODOLOGY - HYPOTHESIS #1 DATA

Since protocol and "non-protocol" techniques for collection were to be compared, both techniques were performed on the same day in quick succession: first the non-protocol, then the protocol technique.

Non-protocol sampling consisted of bailing the monitoring well dry, waiting approximately 2 to 3 hours, and then removing the sample. The sample was neither filtered nor preserved with acid in the field.

Established protocol for sample collection requires successive bailing of the groundwater monitoring well to remove a specific volume of water. After recovery, the sample is removed, filtered on-site with a 45 micron paper filter and preserved with nitric acid. However, for the purpose of the investigation, a "simulated" protocol was developed in order to reduce field time for the investigation. ("Simulated" protocol sample collection, approved by WAWM, consists of successive bailing of the monitoring well, subjecting the bailed water to field tests for specific conductance, pH and temperature. Continued bailing and testing is repeated until a steady-state is achieved for the three field test parameters. When steady-state is reached, a sample is collected, immediately filtered, preserved with nitric acid and transported to the laboratory for analysis.)

As agreed between WAWM and CCASWA, data requirements consisted of one set of samples from the single monitoring well on each of four successive months.

After both samples were delivered to the laboratory, the non-protocol sample was preserved with acid prior to analysis. Standard laboratory analytical procedures for determining concentration of lead were used in order to obtain two sets of data for comparison.

METHODOLOGY - HYPOTHESIS #2 DATA

In order to test the second hypothesis, that there is no trend for increasing lead concentration, data consisted of all prior reported results of lead concentration from non-protocol sampling conducted at the monitoring well since the lead constituent became a required parameter for testing and reporting.

HYPOTHESIS #1 ANALYSIS

Statistical analysis of certainty on confidence interval of data pairs for non-protocol minus protocol samples.

Hypothesis Test - Differences

H_0: (Non-protocol - protocol) ≤ 0 implies no difference in sampling technique

H_1: (Non-protocol - protocol) >0 implies a difference in sampling
Degree of confidence set at 90%: use $N = 3$, for $\alpha = 95\%$, $t = 2.353$ (t-statistic)

Data & Calculations

Lead Concentrations (mg/1)

Non-Protocol Sampling	Protocol Sampling	Difference (D)
0.06	0.01	0.05
0.02	0.01	0.01
0.05	0.01	0.04
0.02	0.01	0.01
		Σ0.11
		D 0.0275

$$\text{s of diff} = \left(\left[\sum D^2 - \frac{(\sum \overline{D})^2}{N}\right]/N-1\right)^{1/2}$$

$$= \left(\left[0.0043 - \frac{(.11)^2}{3}\right]/2\right)^{1/2}$$

$$= 0.0115$$

$$\text{sd of } \overline{D} = s/\sqrt{N} = 0.0115/\sqrt{3} = 0.0067$$

$$\text{Action Limit} = \overline{D} \pm t\ (\text{sd of } \overline{D}) = 0.0275 \pm 2.353\ (0.0067)$$

Hypothesis #1 Results:

Since the low action limit equals 0.0118, that implies a difference (D) > 0; therefore H_1 is substantiated. Based on the above, accept H_1. There is a 90% certainty that a protocol sample will be at least 0.01 mg/l less than a non-protocol sample.

HYPOTHESIS #2 ANALYSIS

To test the hypothesis that lead concentrations in groundwater samples at monitoring well #2 are not increasing: if it can be shown by regression analysis (lead concentration vs. time) that the slope is negative, then the lead concentration is not increasing.

Hypothesis #2 Test Regression Analysis

Curve fit by regression analysis for linear, exponential and power curves, for all data, also considering one data point (4/81, 0.37 mg/l) an outlier.

Data and Calculations

Date of Sampling	Time (Months)	Pb Concentration (mg/1)
4/80	4	0.17
10/80	10	0.10
4/81	16	0.37
10/81	22	data missing
5/82	29	0.07
10/82	34	0.05

		Note #1		Note #2	
Curve Type	Formula	b slope	r^2*	b (slope)	r^2*
Linear	$Y = a + bx$	-0.0035	0.84	-0.0044	0.18
Exponential	$Y = ae^{bx}$	-0.0346	0.92	-0.0399	0.41
Power	$Y = ax^b$	-0.5120	0.96	-0.4614	0.26

#1 Assuming o.37 mg/l lead concentration is an outlier, then N = 4 samples.

#2 Assuming 0.37 mg/l lead concentration is *not* an outlier, then N = 5 samples.

*regression coefficient

Hypothesis #2 Results:

Based on the above, all slopes are negative; therefore there is no trend for increasing lead concentration.

REGULATORY RESPONSE

The result of the investigation was submitted to WAWM on November 29, 1982. On January 19, 1983, WAWM accepted the study and permitted the continued use of non-protocol sampling, reserving only that WAWM would continue to closely observe continued report ing data. There have been two semi-annual samples analyzed after having been collected by the non-protocol method since the investigation was submitted to WAWM. In both cases, the results of the lead concentration in groundwater have been less than 0.05 mg/l. This is significantly below the 0.10 mg/l used as a threshold limit.

CRITIQUE

The investigation was severely constrained from the standpoint of data collection due primarily to the costs involved and the necessity for reporting the results within a given time frame for WAWM action. Specifically:

Only four data points were available and used to determine the relationship between protocol and non-protocol sampling collection technique.

Although only one parameter was purposely varied (sample collection technique) in the comparison of the protocol and non-protocol sampling, other variables are inherent in the determinant result (lab testing of the data samples), no attempt was made to segregate these variables nor control them any more specifically than required by normal laboratory procedures.

Laboratory test detection limit was only carried to 0.01 mg/l. Only five data points were available and used to determine the lack of tendency for increasing lead concentrations in the groundwater based on the historical non-protocol sampling collection method used. Furthermore, laboratory detection limits in some of the prior lead analyses were set only to 0.1 mg/l.

There is one data point (0.37 mg/l) where it is suspected that the sample was not diluted prior to performing laboratory analysis. If dilution in the laboratory was not performed, it is suspected that the analysis would be incorrect by a factor of 10.

There was a break in data collection continuity in making the correlation for lead concentration trend due to the destruction of the original groundwater monitoring well which was subsequently replaced by a new groundwater monitoring well adjacent to the first.

Despite these obvious shortcomings, in particular the lack of data points which makes the statistical analysis technically inconclusive, there is a strong indication that the results of the analysis warranted the action taken by WAWM—to keep close watch on future ground monitoring results while allowing CCASWA to continue with the time and money saving "non-protocol" technique for collection of groundwater samples.

RECOMMENDATIONS

Conduct further research on the advisability of reducing field-collection time for groundwater monitoring collection techniques at landfills. Significant reduction in field time, and therefore cost, will become increasingly important as Federal and State regulations require ever more frequent and more comprehensive monitoring of groundwater at landfills.

INDICES IDENTIFYING SUBSURFACE MICROBIAL COMMUNITIES THAT ARE ADAPTED TO ORGANIC POLLUTION

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ABSTRACT

The subsurface microbiota and their extracellular excretion products are of primary importance in the maintenance of the ground water resources paricularly when the water is polluted. With the development of quantitative biochemical assays for biomasss, community structure, and metabolic activities of the microbes of the subsurface sediments, it proved possible to search for assays that correlated with exposure to pollution. The subsurface sediments from an abandoned creosote waste deposit showed that exposure to pollution increased the total microbial biomass as measured by the extractable phospholipid; shifted the community structure by decreasing the proportion of gram positive bacteria that form glycerol teichoic acids and induced distinctive changes in the ester-linked phospholipid fatty acids. Pollution of the subsurface sediments caused a shift in the nutritional status to a more balanced growth condition in the unsaturated zone reflected in an increased rate of phospholipid formation relative to the formation of the endogenous storage polymer beta hydroxyalkanoate measured after a short exposure to ^{14}C-acetate. In the saturated zone, contamination induced unbalanced growth.

INTRODUCTION

Ground water is an essential resource that must be protected from pollution. Unfortunately the aquifers on which we depend may be contaminated from a multitude of sources. Recently it has been shown that there is a resident microbial community in the subsurface aquifers that can significantly modify the pollutant composition as plumes move through the sediment (Wilson, 1984). With the development of quantitative methods to describe the biomass, community structure, nutritional status, and metabolic activity of the subsurface microbial community and its extracellular polysaccharide polymers (White, et al., 1983a; 1985) it was possible to begin the search for indices that could be utilized to define the responses of the subsurface microbial community to pollution.

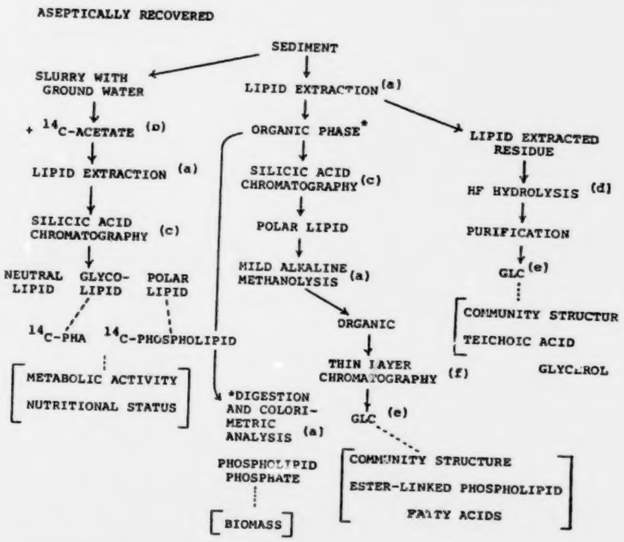
METHODS

Sampling Sites

Uncontaminated sediments from the surface soils and subsurface sediments (up to 10 m deep) were recovered from unconsolidated loamy clays, sometimes containing small gravel deposits, on the margin of a flood plain of a small river at Lula, Oklahoma. The subsurface soil was rich agricultural soil. Contaminated sediments were recovered from a site in Conroe, Texas, on the Gulf coastal plain from an area covered with a poor and highly weathered soil overlying alternating beds of sands and clays of meander belts. A filled lagoon was the source of the organic phenolic wastes from a creosote waste pit that penetrated the meander belt deposits into deeper transmissive sands that overlie an impervious clay. Samples were recovered from an uncontaminated control site (well 14), a site with intermediate contamination (well 16), and a heavily contaminated site (well 15) using the aseptic technique developed at the Robert S. Kerr Environmental Research Laboratory (Wilson, et al., 1983). The sediments were shipped in ice to the laboratories at Florida State University. The analysis was begun within 24 hours of the sampling. A map of the sites and the activity of the microbiota in degrading napththylene, 1-methyl naphthylene, 2-methyl naphthylene, dibenzofuran, fluorene and acenaphthene at this site has been published (Wilson, 1984). The organic contaminants found in the ground water are described elsewhere in this volume (Wang, et al., 1984).

The methods utilized in this study are diagrammed in Table 1. References to the detailed procedures are indicated in the Table. The fatty acids are indicated by the number of carbons: number of double bonds with the position of the unsaturation closest to the hydrophobic end (w) indicated by the number. The c or t indicate the cis or trans orientation of the double bonds.

TABLE 1. ANALYSIS OF CONTAMINATED SUBSURFACE SEDIMENTS



(a) White et al., 1979
(b) Findlay and White, 1984a; 1984b
(c) Gehron and White, 1983
(d) Gehron et al., 1984
(e) Gas liquid chromatography
(f) Bobbie and White, 1980

RESULTS AND DISCUSSION

The key to understanding the effects of pollution on the subsurface microbiota were possible with the provision of samples of the subsurface sediments that were uncontaminated by microbes from the surface. The development of a suite of methods to quantitatively assess the biomass, community structure, nutritional status, and metabolic activities of the ground water aquifer microbiota and the extracellular polymers formed by these microbes was then possible. Microbial biomass can be determined by the analysis of cellular components that are universally distributed. The membrane phospholipids are an example. These phospholipids are a part of every cell membrane, and can be quantitatively extracted and assayed with great sensitivity. Their formation parallels cellular growth, they are present in relatively stable amounts in cells growing under subsurface conditions and in surface sediments have a rapid turnover (White, et al., 1979; Gehron and White, 1983). The community structure can be monitored by the analysis of cellular components that are restricted to subsets of the total microbial community—the "signatures" of specific groups of microbes (White, 1983). Metabolic activities can be monitored by measuring the rates of turnover or synthesis of biomass or "signature" components with labeled precursors. Care must be exercised in the methods by which the labeled precursors are added to sediments or artifacts of disturbance can be generated. This is particularly important in surface sediments with complex gradients of reduced carbon and terminal electron acceptors (Findlay and White, 1984a). We have shown that the formation of endogenous storage lipids which form under conditions of unbalanced growth (expansion without multiplication) has proven to be an excellent measure of nutritional status. The formation and turnover of poly beta-hydroxy alkanoate (PHA) for the prokaryotes (Nickels, et al., 1979; Findlay and White, 1983) and the triglycerides measured as neutral lipid glycerol for the microeukaryotes (Gehron and White, 1982) have provided quantitative measures of the nutritional status. Measuring the ratio of PHA formation to phospholipid fatty acid formation from ^{14}C-acetate has proved an excellent measure of the disturbance artifact in measurements of metabolic activities in sediments (Findlay and White, 1984a; 1984b).

The subsurface aquifer microbiota form polysaccharide exopolymers in large amounts. These polymers contain uronic acids which on reduction with $NaBD_4$ can be assayed quantitatively by GC/MS (Fazio, et al., 1982). The uronic acid components of the polymer can be utilized to define the extracellular localization of these polymers. These polymers tend to be formed in largest amounts under conditions of metabolic stress (Uhlinger and White, 1983).

With these tools in hand it was possible to show that in subsurface clays and sands recovered from 2 to 420 m below the surface from locations in 5 states, a unique subsurface microbial community exists (Gehron and White, 1983; Gehron, et al., 1984; White, et al., 1983a; 1983b, 1984). This community is sparse—the equivalent of 10^6 to 10^7 bacteria per g dry wt. This is some 10-100 fold less than surface sediments by several biomass measures.

The subsurface sediments contain microbes with a unique complement of ester-linked phospholipid fatty acids. The profile of fatty acids differs from surface soils, shallow and deep sea sediments and several types of biofilms. The subsurface sedimentary microbiota are characterized by high proportions of short branched and saturated fatty acids characteristic of bacteria. There is an absence of polyenoic fatty acids characteristic of microeukaryotes. There are high levels of plasmalogen phospholipids, cyclopropane fatty acids, and ester-linked phospholipid hydroxy fatty acids characteristic of facultative and obligatory anaerobic prokaryotic microbes. The ratios of total fatty acids to muramic acid, a unique prokaryotic wall component, indicate the community is exclusively prokaryotic, although some protozoal cysts and yeasts have been recovered.

The subsurface microbiota contains a high proportion of gram positive organisms when compared to surface soils. The organisms of the uncontaminated subsurface sediments are nutritionally stressed as evidenced by the high levels of PHA to phospholipid and the large amounts of uronic acid containing extracellular polymers.

The effects of contamination of the subsurface microbiota by phenolic polycyclic organics from the waste pit of an abandoned creosote plant from Conroe, Texas were examined. Contamination significantly increased the microbial biomass as measured by the extractable phospholipid phosphate (Table 2 A). The most contaminated site had the highest biomass. The highest and lowest means are significantly ($P < 0.05$) different by analysis of variance. The presence of contamination shifts the proportions of gram positive to gram negative bacteria from a gram positive rich microbiota to one progressively more gram negative (Table 2 B). The usual increase in gram positive cells as the depth of the sediment increases (Gehron, et al., 1984) is reversed when the subsurface sediments are contaminated. The very low levels of ribitol teichoic acid (compared to glycerol teichoic acid) seen in the deeper subsurface sediments is preserved in contaminated sediments.

TABLE 3. Ratios of ester-linked phospholipid fatty acid/16.0 that contribute to the discrimination of the control, contaminated and most contaminated subsurface aquifer microbial communities.

		Canonical Discriminant Function Coefficient	
Discriminating variable[a]	F to Remove[b]	Z[c]	
Fatty acid		Function 1	Function 2
Total fatty acids	6.8	29	-7.9
18:2w6	.6	-23.8	9.3
18:1w9c	5.4	-7.4	-0.2
18:1w7c	2.5	4.1	1.1
22:0	14.2	8.3	-0.4
% of total variance		98.8	1.2

[a] Order of entry into stepwise discriminant analysis. Variables not listed did not contribute to the discrimination.

[b] F to remove indicates the penalty for the removal of the variable from the discriminant function.

[c] Standardized coefficient (Z). Those variables with the largest value contribute most to the discrimination by an individual discriminant function.

Possibly the most sensitive and quantitative measures of the shifts in microbial community structure come from the analysis of the ester-linked phospholipid fatty acids (White, 1983). A sensitive analysis of these data, in which the specific fatty acids that contribute most to the differences between samples can be derived from a stepwise discriminant analysis of the proportions of the fatty acids (Federle, et al., 1983). The results of the discriminant analysis of the logarithms of the ratios of ester-linked phospholipid fatty acids to palmitic acid (16:0) between the control and two contaminated subsurface sites are given in Table 3. The graphical representation of this analysis is given in Figure 1. Discriminant function 1 which accounted for 98.8% of the variance clearly differentiated the three subsurface samples. The total fatty acids, the 18:1w7c (a measure of the activity of the anaerobic

TABLE 2. Effects of contamination of the subsurface sedimentary microbiota on the biomass, community structure, metabolic activity and nutritional status.

	Control	Contaminated	Most Contaminated
Site	14	16	15
A.			
Phospholipid (n moles/g dry wt.)	0.6 (0.5)[a]	1.0 (0.8)	1.9 (0.5)
B.			
Ratio teichoic acid glycerol /phospholipid	56 (56)	20.9 (34)	5.4 (1.0)
C.			
Phospholipid synthesis	3200[b,c]	7800[c]	13000[c]
		176 (120)[d]	152 (80)[d]
PHA synthesis	220[c]	270[c]	590[c]
		103 (92)[d]	130 (10)[d]
Ratio phospholipid/PHA	15[c]	29.9[c]	22[c]
		1.7 (1.0)[d]	1.2 (1.2)[d]

[a] Data given as mean (standard deviation).

[b] Total disintegrations per minute per 10 g dry wt sediment after a 20 minute exposure at 25°C in 10 ml well water to 2 Ci sodium acetate-1^{14}C.

[c] Samples from the unsaturated zone.

[d] Samples from the saturated zone.

desaturase pathway) and a long chain saturated fatty acid 22:0 (possibly characteristic of the more complex bacteria like the actinomycetes), were found in highest proportions in the uncontaminated samples. The fatty acids, 18:2w6 and 18:1w9c, were progressively more concentrated in the samples from contaminated sites. Knowing the proportions of the five fatty acids in a given sample allowed assignment to the correct group with an accuracy of 100%.

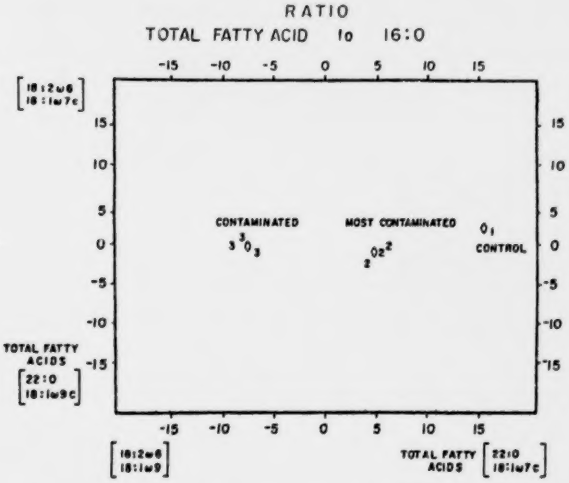


FIGURE 1. Discriminant analysis of ratios of fatty acids to palmitic acid from the phospholipids of the microbiota recovered from uncontaminated (1), contaminated (3), and most contaminated (2) subsurface aquifer sediments.

Contamination of the subsurface environment could also be detected in the metabolic activity and nutritional status of the microbiota. By exposing a slurry of the sediment samples to sodium acetate-^{14}C for 20 minutes, the rates of formation of phospholipid fatty acids could be compared to the rates of formation of the endogenous storage polymer PHA. Balanced growth is indicated by an increase in the ratio of phospholipid synthesis to PHA synthesis; unbalanced growth is indicated by a decrease in this ratio (Nickels, et al., 1979; Findlay and White, 1983; 1984a). Contamination in the saturated zone results in low metabolic activity and unbalanced growth; contamination in the unsaturated and presumably aerated zone results in high metabolic activity and balanced growth (Table 2 C). The disturbance artifact resulting from the suspension of the sediment in a slurry for a 20 minute exposure did not result in cell division as determined by the incorporation of ^{3}H-thymidine into DNA in subtidal estuarine muddy sediments (Findlay and White, unpublished data).

CONCLUSIONS

Despite the complexities in the sediments from the Conroe, Texas site, it proved possible to define some indices that reflect pollution of the subsurface microbial communities. With increasing exposure to the complex phenolic organics of a creosote waste, the biomass of the microbiota increased. The community structure shifted to a more gram negative microbiota with a distinctive pattern of ester-linked phospholipid fatty acids, and the metabolic activity in the unsaturated zone increased with a shift in nutritional status to a more balanced growth condition. The biotransforming activity of the microbiota of these sediments seems to be largely aerobic (Wilson, 1984), suggesting that the catabolism of the polycyclic pollutants induced the shifts in community structure and the marked increase in metabolic activity. The saturated zone sediments from the contaminated sites showed decreased metabolic activity and a nutritional status characteristic of unbalanced growth.

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EFFECT OF NAPHTHALENE ON SOIL AND FRESH-WATER ALGAE

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ABSTRACT

Organisms present in microcommunities may alter the presence or nature of contaminants in soils, ground water, and surface waters. The survival and viability of these microorganisms after exposure to contaminants either from surface spills or seepage can be important in the fate and transport of the contaminants. Representative organisms from the microcommunities may be used to predict or indicate the responses of other organisms of the microcommunity. In this study, the effects of the ubiquitous pollutant naphthalene, a polycyclic aromatic hydrocarbon, on respiration and photosynthetic oxygen evolution of two algae species was determined polarographically.

Chlamydomonas moewusii is a representative eucaryotic soil alga. Exposure of the log phase organism to 15 and 30 ppm naphthalene inhibited both oxygen consumption and evolution. A two hour exposure resulted in an increase in inhibition of both rates.

Chlorella pyrenoidosa is a representative eucaryotic fresh water alga. Oxygen evolution rates were affected by naphthalene in a similar manner as with *Chlamydomonas*. However, with stationary phase cells, exposure to all concentrations inhibited respiration by at least 30%, with rates approaching those of controls for all but cultures exposed to 30 ppm after 2 hours. Respiration by log phase cells was stimulated by exposure to 30 ppm while lower concentrations were inhibitory; rates approached those of controls after 2 hours.

Exposure to the higher concentrations of naphthalene induced morphological variations in both types of algae after 24 and 48 hours.

INTRODUCTION

Naphthalene is a ubiquitous contaminant, found in industrial effluents, water extracts of crude and refined oils (Anderson, et al., 1974), coal tar, sewage plant effluents and even drinking water. It is a member of the class of compounds known as polycyclic aromatic hydrocarbons, which are largely man-made, often toxic, and are entering the environment in increasing amounts with unknown consequences (Pucknat, 1981). Naphthalene has a water solubility of 30 ppm and has demonstrated an acute and chronic toxicity for "fresh water aquatic life" of 2.3 and .6 ppm, respectively (U.S.E.P.A., 1980). In addition, it has been shown to inhibit oxygen consumption of *Daphnia magna* (Crider, et al., 1982), isolated mitochondria and tissue culture cells (Harmon and Sanborn, 1982), and to interact at the molecular level with ubiquinone (Struble and Harmon, 1983), an essential component of the electron transport chain of mitochondrial respiration as well as photosynthesis.

Chlorella pyrenoidosa is a representative fresh water alga while *Chlamydomonas moewusii* is a typical soil alga. The survival and responses of these organisms following contamination of ground or other waters by surface spills, seepage, or other means could be used as an indication of the effect of the contaminant on other soil and water organisms. Microbial activity is responsible for the majority of breakdown of materials applied to the soil and is essential for soil "health" (Burges and Raw, 1967). Any disruption of the "normal" microecology, either through reductions in primary production, blooms, alteration of metabolic activities, or die-offs may alter the fate and transport of substances applied to the soil (or water). Thus the response of these organisms to naphthalene will be investigated to determine the effects on these particular organisms and to examine them as possible indicator species of the "health" and vitality of the micro-environment and its ability to alter or remove pollutants.

MATERIALS AND METHODS

Chlorella pyrenoidosa and *Chlamydomonas moewusii* cultures were the generous gift of Dr. David Francko of Oklahoma State University. Cultures were purified by the standard microbial method of serial transfer on selective and differential media and were maintained in an axenic condition in liquid Moss Media (Moss, 1972) modified by deletion of $Ca(NO_3)_2$, Na_2SiO_3, and NH_4 Cl with addition of 7.21 g/l KNO_3 and 2.6 g/100 ml tricine buffer. The cultures were grown at 25° on a 12/12 hour light/dark cycle to insure synchronous growth (Bernstein, 1960; and Soeder and Ried, 1962). During the light phase, the organisms were exposed to 750 μ Einstein sec^{-1}M^{-2}.

Consumption and evolution of oxygen by the algae were determined polarographically at 25° in a water jacketed chamber using a Clark electrode. A $CuS0_4$ solution was used as a heat sink. To make the determinations, an aliquot of cells in the desired phase was added to the chamber; oxygen consumption was determined in the dark. Actinic illumination, 8,000 μ Einsteins sec^{-1}M^{-2}, was then used to initiate oxygen evolution.

Naphthalene was dissolved, fresh daily, in absolute ethanol and added to cells already in the oxygen chamber for acute type assays. Response of the organisms were assayed as above; controls contained the same volume of ethanol only. For chronic exposures, naphthalene in absolute ethanol was first filter-sterilized and then added in equal aliquots, aseptically, to cultures in the desired phase. Cultures were incubated under the conditions described above and assayed after the desired length of exposure. Controls contained an equal volume of sterilized ethanol added to cultures of the same cell density and phase which were then treated exactly as the naphthalene exposed cultures. All results were determined as percentage inhibition of respiration and oxygen consumption versus the appropriate ethanol control. As respiratory and apparent photosynthetic rates were found normally to vary as much as 20% in both non-toxicated and control cultures within the course of one day or trial, only variations greater than 20% were considered to be significant.

Morphological variations of naphthalene-exposed cells and ethanol-exposed cells were determined using a Nikon inverted phase contrast microscope at 1000 power (oil immersion).

RESULTS AND DISCUSSION

The effects of naphthalene on respiration and light induced oxygen evolution (apparent photosynthesis) of *Chlorella pyrenoidosa* in stationary phase were found to be reproduceable from trial to trial and season to season. Acute exposure caused a stimulation of oxygen consumption by the cells of 30% or greater at all concentrations (Table 1). However, after two hours of exposure in an open system, respiration was affected only slightly by concentrations other than 30 ppm (59% inhibition).

Naphthalene exposure also affected the rate of apparent photosynthesis of the cells. Acute exposure to 15 ppm or greater naphthalene inhibited the rate approximately 50% (Table 2) while 7.5 ppm induced a 21% inhibition. After two hours of exposure to 30 ppm in an open system, inhibition had increased to 87% while the lower concentrations of 7.5 and 15 ppm displayed a 30% inhibition.

Cells in stationary phase apparently recover quite rapidly from naphthalene toxication. The respiratory rate of cells two hours after exposure in an open system to all concentrations except 30 ppm were similar to that of the control cells. Cultures assayed 24 hours or 7 days after exposure showed little deviation from control rates at all con-

Table 1

Effect of Naphthalene on Respiration in Stationary Phase

Chlorella pyrenoidosa

Exposure	Typical Control Value	3.75 ppm	% Inhibition 7.5 ppm	15ppm	30ppm
Acute	2.0×10^{-7}				
2 hour	2.6×10^{-7}	+51	+30	+58*	+58
24 hour	1.4×10^{-7}	+ 2	+18	+ 2	59
7 day	1.3×10^{-7}	+ 6	+11	4	+ 4
		9	6	19	+15

+ indicates stimulation of rate

* nmole O_2/cell/min

centrations tested (Table 1). After 24 hours or 7 days, photosynthetic activity was also not significantly perturbed from that displayed by control cultures (Table 2).

Table 2

Effect of Napthalene on Apparent Photosynthesis in Stationary Phase

Chlorella pyrenoidosa

Exposure	Typical Control Value*	3.75 ppm	% Inhibition 7.5 ppm	15ppm	30ppm
Acute	1.1×10^{-6}	+ 2	21	50	47
2 hour	1.6×10^{-6}	+10	30	30	87
24 hour	5.8×10^{-7}	4	5	7	17
7 day	3.0×10^{-7}	6	10	6	+18

+ indicates stimulation of rate

* nmole O_2/cell/min

The response of log phase *Chlorella pyrenoidosa* cells to exposure to naphthalene is different than that displayed by stationary phase cells. Acute exposure to 7.5 and 15 ppm naphthalene inhibited respiration more than 20% while exposure to 30 ppm unexplainedly stimulated oxygen consumption more than 40% (Table 3). However, two hours after exposure in an open system, respiration had virtually returned to control rate at all concentrations.

Table 3

Effect of Naphthalene on Respiration and Apparent Photosynthesis in Log Phase

Chlorella pyrenoidosa

Assay	Exposure	Typical Control Value*	3.75 ppm	% Inhibition 7.5 ppm	15ppm	30ppm
Respiration	Acute	8.3×10^{-7}	18	25	30	+43
Respiration	2 hour	6.7×10^{-7}	+ 7	+ 5	+ 3	16
Photosynthesis	Acute	1.8×10^{-6}	4	10	23	48
Photosynthesis	2 hour	4.7×10^{-6}	+ 4	+ 6	52	73

+ indicates stimulation of rate

* nmole O_2/cell/min

Acute exposure of log phase cells to 15 and 30 ppm naphthalene inhibited apparent photosynthesis by 23% and 48% respectively (Table 3). After a two hour exposure, inhibition had increased to 52% and 73%, respectively.

Data obtained from chronic exposure trials with log phase *Chlorella* cells were not reproduceable internally or from day to day. Control cultures displayed widely varying rates. This unpredictability is not totally unexpected as the responses of algal cells in the phase of rapid growth and division have been found to often vary widely. For example, the production and extracellular release of cyclic AMP by *Anabaena flos-aquae* was found to vary greatly "within and between active growth phase and stationary phase" (Francko and Wetzel, 1981). In a later study, levels of cyclic AMP were found to vary more in the actively growing cells than in stationary phase cells (Francko, 1984). That levels of the cyclic nucleotides may either influence or be influenced by the metabolic processes of the cell suggests that data obtained with log phase algal cells may be inherently less reproduceable than data with stationary phase ones.

Morphological changes were observed upon exposure of *Chlorella pyrenoidosa* cultures to naphthalene. At both 24 and 48 hours after exposure, cells exposed to 30 ppm displayed greater size and shape variation than control cells. At 24 hours some cells were irregularly shaped, while at 48 hours some cells displayed internal disorganization of components as compared to control cells. Cells exposed to lower concentrations showed similar effects but with decreasing frequency and severity with decreasing concentrations of naphthalene. Cells exposed to 4 ppm for 24 hours and to 4 or 8 ppm for 48 hours were indistinguishable from control cells, indicating that morphological changes, like metaboliic changes, are reversible.

The effects of naphthalene on respiration and apparent photosynthesis by *Chlamydomonas moewusii* were also investigated. Preliminary results with stationary cells indicate that these algae are more resistant to acute exposure than are the *Chlorella*. Only exposure to 30 ppm naphthalene elicited a significant response (33% inhibition) in apparent photosynthesis (Table 4), while 15 ppm and 30 ppm stimulated respiration by less than 25%.

Table 4

Effect of Naphthalene on Respiration and Apparent Photosynthesis in Log Phase

Chlamydomonas moewusii

Assay	Exposure	Typical Control Value*	3.75 ppm	% Inhibition 7.5 ppm	15ppm	30ppm
Stationary phase Respiration	Acute	1.0×10^{-6}	+11	+12	+22	+23
Stationary phase Photosynthesis	Acute	1.3×10^{-6}	+16	+13	+14	33
Log Phase Respiration	Acute	1.9×10^{-6}	+ 4	7	16	47
Log Phase Respiration	2 hour	1.8×10^{-6}	+ 9	+24	28	42
Log Phase Photosynthesis	Acute	6.6×10^{-6}	5	34	36	54
Log Phase Photosynthesis	2 hour	7.0×10^{-6}	16	16	79	85

+ indicates stimulation of rate

* nmole O_2/cell/min

Log phase *Chlamydomonas moewusii* appear more sensitive to acute exposure than are stationary phase cells. Respiration was inhibited 47% by exposure to 30 ppm naphthalene while photosynthesis was inhibited around 35% by exposure to 7.5 and 15 ppm, and 54% by exposure to 30 ppm naphthalene. Preliminary data suggest that log phase *Chlamydomonas* cells are more perturbed after a two hour exposure in an open system than are *Chlorella* cells. Log phase *Chlamydomonas* cells exposed to 15 and 30 ppm displayed 79% and 85% inhibitions of photosynthesis while respiration was inhibited by 28% and 42% respectively.

The morphology of these cells was also affected by exposure to naphthalene. The most noticeable effect was the loss of flagella and cessation of movement by cells exposed to 30 ppm naphthalene. This effect has been reported in *Chlamydomonas angulosa* at 16 ppm by Soto, et al. (1979). Cells exposed to lower concentrations moved less rapidly than control cells. A few cells were stationary but did not appear to have lost their flagella.

As with log phase *Chlorella* cells, *Chlamydomonas* cultures in log phase exposed for 24 or 48 hours in an open system displayed unpredictable and irreproduceable responses; control cultures (exposed to ethanol) were also not internally reproduceable. Bernstein (1964), working with *Chlamydomonas moewusii*, suggests that in synchronous cultures, stationary phase cells may be more limited by culture conditions (less light, depletion of nutrients, etc.) than log phase cells. The stationary phase cells would be reduced to a more "basal" level of production, and hence be less variable than log phase cells.

CONCLUSIONS

Exposure of stationary or log phase *Chlorella pyrenoidosa* and *Chlamydomonas moewusii* to naphthalene affected both respiration and apparent photosynthesis in the algae. However, the two types of algae in different phases displayed varying responses in both degree and kind. Respiration and photosynthesis by stationary phase *Chlorella* was the most profoundly affected by an acute exposure while stationary phase *Chlamydomonas* was the least inhibited.

It is interesting that the acute EC_{50} for photosynthesis and respiration in stationary phase *Chlorella* for exposure to naphthalene correlates well with that reported (15 ppm) by Harmon and Sanborn (1982) for isolated mitochondria and three types of tissue culture cells. However, log phase cells of both types of algae as well as stationary phase *Chlamydomonas* appear more resistant to acute exposure to naphthalene. This observed phase-dependent sensitivity may be somehow related to the overall metabolic rate of the cell. In *Chlorella*, stationary phase cells exhibit approximately 1.5-2 fold less respiratory and photosynthetic activity compared to log phase cells; in *Chlamydomonas*, activity in log phase cells is at least 2-fold greater than in stationary phase cells. This finding suggests that sensitivity to naphthalene may depend on the "turn-over" of component(s), such as quinone, in the cell. All data has been normalized on a per cell basis. If each cell in either phase contain the same number of functional photosynthetic or respiratory chains, but each chain operates at different rates, the level of oxidized or reduced quinone (and hence the extent of inhibition to naphthalene) will be different for the two phases. Struble and Harmon (1983) were able to demonstrate an effect of naphthalene on the oxidized quinone form (due to the absence of spectrum of the quinol form). Thus, stationary phase cells, in which less 0_2 is consumed by mitochondria, would contain more reduced quinol than the stationary phase cells and be inhibited less by naphthalene as observed.

After a two hour exposure (allowing time both for naphthalene to enter cells and organelles as well as for detoxification mechanisms to begin action) respiration by stationary *Chlorella* approached control rates for all but those cultures exposed to 30 ppm. Photosynthesis, however, was affected more. After 24 hours, all rates approached those of controls. As cultures were exposed in an open system, naphthalene volatilization was constantly occurring; less than 15% of the original concentration of toxicant was present after 24 hours. Log phase cells displayed the same type of response; respiration after 2 hours approached control rates while photosynthesis was significantly more affected. In log phase *Chlamydomonas*, both respiration and photosynthesis were altered more after a 2 hour exposure than during an acute trial. The cells apparently recover from naphthalene toxication, although their morphology remains altered 24 hours after exposure to higher concentrations.

These results, especially the large inhibitions of photosynthesis after 2 hour exposures, indicate that naphthalene does perturb the respiratory and photosynthetic capacity of the two types of algae, at least temporarily. As these two processes are essential for generation and conservation of energy by the cells and hence are vital for metabolism, these perturbations may have serious consequences for the cells, including reducing their capacity to remove or alter toxicants applied to soil or waters. Effects on these algae, in addition to the previously mentioned inhibitions of respiration by isolated mitochondria and tissue culture cells, indicate potential for disturbances of the energy generation and conservation mechanisms in other organisms important in maintaining soil and water microecology and "health".

Of equal importance in this study is the demonstration that the life cycle stage of the cells plays a strong role in toxicity measurement; actively growing and metabolizing cells will be far more sensitive to some toxicants than stationary phase, "dormant", or "resting" cells. Ecosystem studies must take this parameter into account in the assessment of hazardous effects.

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